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A

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A DICTIONARY

OF

CHEMISTRY

AND THE

ALLIED BRANCHES OF OTHER SCIENCES.

BY

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EDITOR OF

'THE JOURNAL OF THE CHEMICAL SOCIETY.'

ASSISTED BY EMINENT CONTRIBUTORS.

IN FIVE VOLUMES.

VOL. I.

ABICHITE—CONGLOMERATE.

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1868.

PREFACE.

THIS WORK was originally intended as a New Edition of Ure's *Dictionary of Chemistry and Mineralogy*; but the great changes made in chemical science since the publication of the last edition of that Dictionary (1831)—changes, not merely consisting in the addition of new discoveries, but involving a complete revolution in the mode of viewing and expressing chemical reactions—have rendered it almost impossible to adapt any matter written so long ago to the existing requirements of the science. The present must therefore be regarded as essentially a new work, in which only a few articles of Ure's *Dictionary* are retained, chiefly of a descriptive character. In compiling it, the Editor has freely availed himself of the stores of information in Gmelin's "Handbook," Gerhardt's "Chimie Organique," Rose's "Traité d'Analyse Chimique," Dana's "Mineralogy," Rammelsberg's "Mineralchemie," the "Handwörterbuch der Chemie," &c.; and has endeavoured, by careful consultation of original memoirs, to bring the treatment of each subject down to the present time. He has also been fortunate in obtaining the co-operation of several chemists of acknowledged ability and eminence, who have kindly contributed articles on subjects to which they have paid special attention:—a List of their names is given on the next leaf.

The work is essentially a Dictionary of Scientific Chemistry, and is intended as a Companion to the New Edition of Ure's *Dictionary of Arts, Manufactures, and Mines*, to which therefore reference is, for the most part, made for the details of manufacturing operations; but those branches of chemical manufacture which have come into existence, or have received important developements, since the publication of that work, are described in this Dictionary as fully as its limits will allow, and in all cases explanations are given of the principles on which manufacturing processes are conducted, and the chemical changes which they involve. Particular attention has also been given to the description of processes of Analysis, both qualitative and quantitative.

In order that the work may, as far as possible, truly represent the present state of scientific chemistry, it has been found absolutely necessary to make the modern or "unitary" scale of atomic weights the basis of the system of notation and mode of exposition adopted. Especial care has, however, been taken that the treatment of all Articles which are likely to be consulted, for the sake of practical information, by manufacturers, or others not exclusively occupied in chemical pursuits, shall be such as to make them readily intelligible to all who possess a general knowledge of chemistry, though they may not have followed closely the recent developements of the theoretical parts of the science. Hence, in all such Articles (as ACETIC ACID, ANTIMONY, COPPER, &c.) the formulæ are given according to the old notation (printed for distinction, in *Italics*), as well as according to that adopted in the rest of the work.

Temperatures are given on the *centigrade* scale, excepting when the contrary is expressly stated.

HENRY WATTS.

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⁂ Articles communicated by the several contributors are signed with their initals; articles taken from URE's *Dictionary of Chemistry* (fourth edition, 1831) are signed with the letter U; those which have no signature are by the Editor.

DICTIONARY OF CHEMISTRY.

A

ABICHITE. (*Aphanesite, Strahlerz, Strahlenkupfer.*) A native arsenate of copper, found chiefly associated with other copper ores and veins in Cornwall, and in the Hartz. The crystals belong to the monoclinic or oblique prismatic system, but they seldom exhibit any definite shape, being aggregated in radiating groups, or disposed, as extremely minute individuals, in cavities of quartz. Sp. gr. 4·2 to 4·4. Hardness, 2·5 to 3. Translucent or opaque, with vitreous lustre. Colour, blackish green inclining to blue. Streak, bluish-green. Dana (Mineralogy, ii. p. 428) gives for this mineral the formula $3CuO.AsO^5 + 3CuO.HO$*, or $AsCu^3O^4 + Cu^2HO^2$, deduced from the analyses of Rammelsberg and Damour. L. Gmelin (Handb. v. 471) gives the formula $5CuO.AsO^5 + 5HO$, deduced from the analysis of Chenevix, who found 54 per cent. of protoxide of copper, 30 per cent. of anhydrous arsenic acid, and 16 per cent. of water.

ABIETIC ACID. $C^{20}H^{30}O$? When Strasburg or Canadian turpentine (obtained respectively from *Abies picea* and *Abies balsamea,*) is distilled with water; the residue exhausted with absolute alcohol; the solution evaporated to dryness; the residual resin boiled with twice its weight of solution of carbonate of potassium; the alkaline liquid poured off; and the residue, which is a mixture of abietin and abietate of potassium, treated with 30 times its weight of water, — abietin separates in the crystalline form, while abietate of potassium remains in solution. This solution may be decomposed by sulphuric or hydrochloric acid, and the precipitated abietic acid purified by digestion in hot aqueous ammonia. As thus obtained, it is a resinous mass which dissolves easily in alcohol, ether and volatile oils, forming acid solutions, from which it separates in the crystalline state. At 55° it becomes soft and translucent. Its barium-salt is said to contain 191 parts of the acid to 76·6 parts (1 at.) of baryta. The acid is perhaps identical with sylvic or pymaric acid. (Caillot, J. Pharm. xvi. 436; Gerh. iii. 656.)

ABIETIN. Prepared as above. It is a tasteless inodorous resin, insoluble in water, soluble in alcohol, especially at the boiling heat, also in ether, rock-oil, and strong acetic acid, and separates in the crystalline form from these solutions by evaporation. It melts when heated, and solidifies in a crystalline mass on cooling. It is not acted upon by caustic potash. (Caillot.)

ABRAZITE. (*Gismondin.*) A mineral of the zeolite family, containing, according to Marignac's analysis:

$$8(CaKO.SiO^2) + 4Al^4O^3.SiO^2 + 18H^2O; \qquad [Si=28;\ O=16].$$
$$\text{or } 2(CaO.KO).SiO^3 + 2(Al^2O^3.SiO^3) + 9HO; \qquad [Si=21;\ O=8].$$

It is found on Vesuvius, at Aci-Castello in Sicily, and at Capo di Bove, near Rome. It occurs united with Phillipsite in quadratic octahedrons, generally aggregated in

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* The atomic weights adopted in this work are those of the unitary system (H = 1; O = 16; S = 32; C = 12). Frequently, however, the formulæ of compounds will likewise be given according to the dualistic system ($O = 8$, $S = 16$, $C = 6$); and for distinction, these latter formulæ will be printed in italics.

masses. Transparent or translucent, with greyish-white colour. Hardness = 4·5. Sp. gr. = 2·265. Gives off one-third of its water at 100°. Easily dissolves in acids and gelatinises. It was formerly supposed to be a variety of Phillipsite or lime-harmotome; but it differs from harmotome in composition as well as in crystalline form, the latter mineral crystallising in the dimetric system. (Dana, ii. 322.)

ABSINTHIN. $C^{16}H^{22}O^{5}$. The bitter principle of wormwood (*Artemisia absinthium*). It is prepared in the pure state, according to Luck, by exhausting the leaves of wormwood with alcohol, evaporating the extract to the consistence of a syrup, and agitating with ether. This ethereal solution is evaporated to dryness, and the residue treated with water containing a little ammonia, which dissolves the resin, and leaves the absinthin nearly pure. To complete the purification, it is digested with weak hydrochloric acid, washed with water, dissolved in alcohol, and treated with acetate of lead, as long as a precipitate is formed. After the removal of this precipitate by filtration, the excess of lead is precipitated by sulphuretted hydrogen, and the solution is evaporated. The absinthin then remains as a hard, confusedly crystalline mass, possessing an extremely bitter taste. It is but slightly soluble in water, very soluble in alcohol, and less so in ether. It possesses distinctly acid characters, and is dissolved by potash and ammonia. (Mein, Ann. Ch. Pharm. viii. 61; Luck, ibid. lxxviii. 87; Gerh. iv. 258.)

ABSORPTION OF GASES. See Gases.

ACACIN, or **ACACIA-GUM.** Known in commerce as *gum-arabic.* See Arabin and Gum.

ACADIOLITE. A variety of chabasite from New Caledonia, distinguished by its large amount of alkali. (Hayes, Sill. Am. J. [2] I. 122.)

ACAJOU. The stem of the Acajou or Cashew-nut tree, *Anacardium occidentale*, yields a yellow gummy substance, sparingly soluble in water, which is a mixture of ordinary gum and bassorin. The pericarp of the nuts of the same tree contains a large quantity of a red-brown resinous substance, which produces inflammation and blistering of the skin. It may be extracted by ether, and the ethereal solution when slowly evaporated, leaves a residue consisting of a network of small crystals of anacardic acid, soaked in an oily liquid called cardol, to which the resin owes its acrid properties (Städeler, Ann. Ch. Pharm. lxiii. 137). The name acajou is also applied to a gum and resin obtained from the stem of the mahogany-tree. The gum resembles that of the cherry-tree.

ACAROID RESIN. The resin of *Xanthorrhea hastilis*, a liliaceous tree growing in New Holland; also called resin of Botany Bay. It has a yellow colour, an agreeable odour, and is soluble in alcohol, ether, and caustic potash. Its potash-solution treated with hydrochloric acid deposits benzoic and cinnamic acids. Nitric acid converts it into picric acid, and so readily, that this resin appears to be the best raw material for obtaining picric acid. By distillation, the resin yields a light neutral oil, which appears to be a mixture of benzol and cinnamol, and a heavy acid oil, consisting of hydrate of phenyl, mixed with small quantities of benzoic and cinnamic acids. (Stenhouse, Ann. Ch. Pharm. lvii. 84.)

ACECHLORIDE OF PLATINUM. See Acetone, *Decompositions* (p. 29).

ACEDIAMINE. $C^{2}H^{6}N^{2}$. When hydrochlorate of acetamide is heated in a sealed tube to 180°—200°, and the product afterwards distilled, or when acetamide is distilled in a stream of dry hydrochloric acid gas, several volatile products pass over, and a residue is left consisting of hydrochlorate of acediamine, mixed with sal-ammoniac. (See Acetamide):

$$\underbrace{2C^{2}H^{5}NO}_{\text{Acetamide.}} + HCl = \underbrace{C^{2}H^{6}N^{2}.\ HCl}_{\substack{\text{Hydrochlorate}\\ \text{of acediamine.}}} + \underbrace{C^{2}H^{4}O^{2}}_{\text{Acetic acid.}}.$$

Alcohol extracts the hydrochlorate of acediamine from this residue, and deposits it by spontaneous evaporation in prismatic crystals, which may be completely freed from adhering sal-ammoniac by solution in a mixture of alcohol and ether, and evaporation in vacuo. The hydrochlorate decomposed by sulphate of silver, yields the *sulphate of acediamine* $(C^{2}H^{6}N^{2})^{2}.\ SO^{4}H^{2}$, which crystallises in colourless nacreous laminæ, easily soluble in water. The aqueous solution of the hydrochlorate mixed with dichloride of platinum yields the *chloroplatinate of acediamine*, $C^{2}H^{6}N^{2}.\ HCl.\ PtCl^{2}$, in rather large, hard, yellowish red prisms.

Acediamine is very unstable, and cannot be obtained in the free state. When the sulphate or hydrochlorate is heated with potash or baryta, ammonia is given off, and an acetate of the alkali is produced:

$$C^{2}H^{6}N^{2} + 2H^{2}O = C^{2}H^{4}O^{2} + 2NH^{3}.$$

Acediamine may be regarded as ammonia in which 1 at. H is replaced by the monatomic radical C^2H^4N (azethyl), its rational formula being then $N.H^2.C^2H^4N$ or as a double molecule of ammonia, N^2H^6, having 3 at. H replaced by the triatomic radical C^2H^3, making its formula $N^2.H^3.(C^2H^3)'''$ It bears the same relation to acetamide as ethylamine to alcohol:

$$C^2H^6O + NH^3 = C^2H^7N + H^2O: \text{ and } C^2H^3NO + NH^3 = C^2H^6N^2 + H^2O.$$

(Strecker, Ann. Pharm. ciii. 328.)

ACEPHOSGENIC ACID and **ACEPHOSSIC ACID.** Compounds produced by the action of phosphorus on acetone (see page 28).

ACETAL. $C^6H^{14}O^2$.—[Gm. ix. 38; Gerh. ii. 268.] A product of the oxidation of alcohol, first observed by Döbereiner, more fully examined by Liebig (Ann. Ch. Pharm. v. 25; xiv. 156), still further by Stas (Ann. Ch. Phys. [3] xix. 146), who first correctly determined its empirical formula, and finally by Wurtz (Compt. rend. xlviii. 478; Ann. Ch. Phys. [3] xlviii. 370; Ann. Ch. Pharm. cviii. 84). It is also obtained from aldehyde. (Wurtz and Frapolli, Ann. Ch. Pharm. cvii. 228.)

Preparation. I. From *Alcohol.* 1. By the imperfect oxidation of alcohol, under the influence of platinum-black. Pieces of pumice-stone previously washed and ignited are moistened with nearly absolute alcohol, and placed at the bottom of a large wide-necked flask, which is then filled up with capsules containing platinum-black, covered with a glass plate, and exposed to a temperature of 20°, till the whole of the alcohol is acidified. Alcohol of 60 per cent. is then poured into the flask, in quantity not quite sufficient to cover the pumice-stones, and the flask left to itself for two or three weeks in a room at a temperature of 20°, the glass plate being removed from time to time to admit fresh air. The thickish liquid is then drawn off, and the same process repeated with fresh alcohol, till several quarts of thickish acid liquid are obtained. This liquid is neutralised with carbonate of potassium, saturated with chloride of calcium and distilled, and the first fourth of the distillate is saturated with fused chloride of calcium, which separates from it a mixture of alcohol, acetic-ether, aldehyde, and acetal. The aldehyde is removed by distillation over the water-bath; the residue treated with strong potash to decompose the acetic ether; the alcohol removed by washing with water; and the remaining liquid, the acetal, dried over chloride of calcium and rectified. (Stas.)

2. By distilling alcohol with dilute sulphuric acid and peroxide of manganese. A mixture of 2 parts alcohol, 3 parts peroxide of manganese, 3 parts sulphuric acid, and 2 parts water (the proportions given by Liebig for the preparation of aldehyde), is subjected to distillation as soon as the frothing which first ensues has ceased; 3 parts of liquid are distilled off; the distillate is rectified; and the portion which goes over at 80° is collected apart from that which distils between 80° and 95°. The first portion is mixed with chloride of calcium and rectified, the distillate obtained below 60° chiefly consisting of aldehyde, while above 60° a product is obtained, which, when treated with a strong solution of chloride of calcium, yields an ethereal liquid. The portion of the former liquid which came over between 80° and 95°, is also rectified, and the first portion of the resulting distillate treated with strong solution of chloride of calcium, whereupon it likewise yields an ethereal liquid. These ethereal liquids, containing aldehyde, acetic ether, &c. and acetal are united, and shaken with caustic potash to resinise the aldehyde and decompose the acetic ether. The brown liquid which floats upon the potash-solution is separated and distilled; the distillate again mixed with chloride of calcium; the liquid thus separated is heated to 100° for twenty-four hours with twice its volume of caustic potash in a sealed tube; the lower stratum is rectified; the distillate again shaken with chloride of calcium; and the separated liquid is digested with pulverised chloride of calcium, and submitted to simple rectification. Pure acetal then distils over from 100° to 105°. (Wurtz.)

3. By the action of chlorine upon alcohol, acetal being indeed the principal product of that reaction, so long as no substitution-products are formed:

$$3C^2H^6O + 2Cl = C^6H^{14}O^2 + 2HCl + H^2O.$$

Chlorine is passed through 80 per cent. alcohol cooled to between 10° and 15°, till a portion becomes turbid on the addition of water, indicating the formation of substitution-products. One fourth of the strongly acid liquid is then distilled off; the distillate neutralised with chalk; one fourth again distilled off; and the distillate, consisting of alcohol, acetic ether, aldehyde and acetal, treated as above to separate the acetal. (Stas.)

According to Lieben (Ann. Ch. Phys. [3] lii. 313), the chief products of the action of chlorine on alcohol of 80 per cent. are monochloracetal and dichloracetal. (p. 5.)

II. From *Aldehyde.* 1. By treating aldehyde with pentabromide of phosphorus, whereby it is converted into *bromide of ethylidene* $C^2H^4Br^2$ (a compound isomeric with bromide of ethylene), and acting on this compound with ethylate of sodium.

$$C^2H^4Br^2 + 2C^2H^5NaO = 2NaBr + 2C^6H^{14}O^2.$$

This mode of preparation is, however, very troublesome, on account of the difficulty of obtaining the bromide of ethylidene. Chloride of ethylidene $C^2H^4Cl^2$, (produced by the action of pentachloride of phosphorus on aldehyde) does not appear to yield acetal when treated with ethylate of sodium.

2. By passing hydrochloric acid gas into a mixture of 1 vol. aldehyde and 2 vols. absolute alcohol immersed in a freezing mixture, whereby the compound C^4H^9ClO is obtained in the form of an ethereal liquid floating on aqueous hydrochloric acid,—and treating this compound with ethylate of sodium:

$$\begin{aligned} & C^2H^4O + C^2H^6O + HCl = C^4H^9ClO + H^2O \\ \text{and}\quad & C^4H^9ClO + C^2H^5NaO = NaCl + C^6H^{14}O^2 \end{aligned}$$

(Wurtz and Frapolli, Compt. rend. xlvii. 418; Ann. Ch. Pharm. cviii. 223.)

Properties.—Pure acetal is a colourless liquid, less mobile than ether, having a peculiar agreeable odour and a refreshing taste, with an after-taste like that of hazel nuts. Sp. gr. 0·821 at 22·4. Boils at about 105° C., with the barometer at 0·768 met. Vapour density = 4·141.

It dissolves in eighteen times its volume of water at ordinary temperatures, the solubility increasing as the temperature rises. From the aqueous solution it is separated by chloride of calcium and other soluble salts. Ether and alcohol dissolve it in all proportions.

Decompositions.—1. Acetal is not altered by mere exposure to the air, but in contact with platinum-black it is quickly converted, first into aldehyde, and then into acetic acid:

$$\underbrace{C^6H^{14}O^2}_{\text{Acetal.}} + 2O = \underbrace{3C^2H^4O}_{\text{Aldehyde.}} + H^2O.$$

It is likewise oxidised by nitric and by chromic acid. 2. Caustic alkalies do not decompose it, if the air is excluded. 3. Chlorine abstracts hydrogen from it and forms substitution-products. 4. Strong sulphuric acid dissolves and then decomposes it, the mixture turning black. 5. Hydrochloric acid likewise dissolves and blackens it, forming choride of ethyl. 6. Pentachloride of phosphorus acts strongly upon it, forming a large quantity of chloride of ethyl, together with other products. 7. Heated in a sealed tube with several times its weight of glacial acetic acid, it yields acetic ether, more than 1 atom of that compound being formed from 1 atom of acetal.

These reactions tend to show that acetal is an ethyl-compound. Stas regarded it as a compound of 1 at. aldehyde with 1 at. ether:

$$C^2H^4O + C^4H^{10}O = C^6H^{14}O^2;$$

and Wurtz, in his earlier researches on glycol (Compt. rend. xliii. 478), regarded it as glycol $\left.\begin{matrix} C^2H^4 \\ H^2 \end{matrix}\right\} O^2$, in which 2 at. hydrogen are replaced by ethyl $\left.\begin{matrix} C^2H^4 \\ (C^2H^5)^2 \end{matrix}\right\} O^2$. This view of its constitution was corroborated by the result of distilling a mixture of alcohol and wood-spirit with sulphuric acid and peroxide of manganese, whereby a distillate was obtained consisting of *dimethylate of ethylene* $\left.\begin{matrix} C^2H^4 \\ (CH^3)^2 \end{matrix}\right\} O^2$, and methylethylate of ethylene $\left.\begin{matrix} C^2H^4 \\ CH^3.C^2H^5 \end{matrix}\right\} O^2$. Subsequent researches have however shown that acetal is not identical, but only isomeric with diethyl-glycol, or diethylate of ethylene $C^2H^4.(C^2H^5)^2.O^2$. For, when glycol $C^2H^4.H^2.O^2$ is treated with sodium, 1 at. hydrogen is eliminated, and the compound $C^2H^4.NaH.O^2$ is obtained. This compound treated with iodide of ethyl yields *ethylate of ethylene* $C^2H^4.C^2H^5.H.O^2$, whence, by the action of potassium, the compound $C^2H^4.C^2H^5.K.O^2$ is produced; and, lastly, this compound treated with iodide of ethyl yields *diethylate of ethylene* $C^2H^4.(C^2H^5)^2.O^2$. Now this liquid has a specific gravity of 0·7993 at 0° C., and boils at 123·5 C., whereas acetal has a sp. gr. of 0·821 at 22°·4, and boils at 105°, that is to say, 18°·5 lower. Recent experiments by Beilstein (Ann. Ch. Pharm. cxii. 240) seem to indicate that the rational formula of acetal is $C^4H^9O.C^2H^5.O$.

Chloracetals (A. Lieben, Ann. Ch. Phys. [3] lvi. 313). Three of these compounds have been obtained; viz. *mono-*, *di-*, and *tri-chloracetal.* The two former are produced by the action of chlorine on alcohol of ordinary strength (80 per cent.) When the chlorine has been passed through for some time, and the heavy oil which separates on addition of water is washed several times with aqueous chloride of calcium, and submitted to fractional distillation, it begins to boil at 80°, and the boiling point gradually rises to 200°, not, however, remaining stationary at any intermediate point. The portion which distils below 120° consists of aldehyde and compound ethers; that which distils above 120° (which is the larger portion) contains monochloracetal and dichloracetal. On again submitting it to fractional distillation, the greater part goes over between 170° and 185°; this portion consists chiefly of dichloracetal, which may be obtained pure by subsequent rectification. To separate the monochloracetal, the portion of the second distillate boiling below 170°, and the portion of the first distillate which passed over above 120°, are heated for several days with aqueous potash, whereby a watery liquid is obtained, containing chloride and formate of potassium, and an oily liquid consisting chiefly of monochloracetal mixed with dichloracetal; these compounds are finally separated by fractional distillation.

According to Lieben, the product of the action of chlorine on alcohol of ordinary strength does not contain acetal. This is contrary to the statement of Stas, who, in fact, prepared acetal by this very process. Probably the relative quantities of acetal, monochloracetal, and dichloracetal obtained depend on the duration of the action of the chlorine (compare page 3).

Monochloracetal, $C^6H^{13}ClO^2$, is a colourless liquid, having an ethereal aromatic odour, and boiling at about 155°. Vapour-density, by experiment 5·38; by calculation (2 vols.) 5·29. It is perfectly neutral, insoluble in water, soluble in alcohol. It is not attacked by aqueous potash, and does not precipitate nitrate of silver.

Dichloracetal, $C^6H^{12}Cl^2O^2$, is a colourless neutral aromatic liquid of sp. gr. 1·1383 at 14°. Boils at about 180°. Vapour-density, by experiment 6·45; by calculation (2 vols.) 6·435. (Lieben.)

Trichloracetal, $C^6H^{11}Cl^3O^2$, is produced, together with dichloracetal, by the action of chlorine on highly concentrated but not absolute alcohol. (Dumas, Lieben.)

ACETAMIDE. $C^2H^5NO = N.H^2.C^2H^3O$. Produced:

1. By heating acetate of ethyl with strong aqueous ammonia to about 120°:

$$\underbrace{C^2H^3O.C^2H^5.O}_{\text{Acetate of ethyl.}} + NH^3 = \underbrace{NH^2.C^2H^3O}_{\text{Acetamide.}} + \underbrace{C^2H^5.H.O}_{\text{Alcohol.}}$$

2. By the action of ammonia on acetic anhydride:

$$\underbrace{(C^2H^3O)^2O}_{\text{Acetic anhydride.}} + NH^3 = \underbrace{NH^2.C^2H^3O}_{\text{Acetamide.}} + \underbrace{C^2H^3O.H.O}_{\text{Acetic acid.}}$$

3. By distilling acetate of ammonium ($C^2H^4O^2.NH^3 = C^2H^5NO + H^2O$). A large quantity of ammonia is given off at first, then at 160° an acid distillate, consisting chiefly of acid acetate of ammonium; above 160°, a distillate containing acetamide which crystallises in the condensing tube; and above 190° nearly pure acetamide. By saturating glacial acetic acid with dry ammoniacal gas, and then distilling, $\frac{1}{4}$ of the acetic acid may be converted into acetamide. (Kundig, Ann. Ch. Pharm. cv. 277.)

Acetamide is a white crystalline solid, which melts at 78° and boils at 221° or 222°. It deliquesces when exposed to the air, and dissolves readily in water. Heated either with acids or with alkalis, it takes up water, and is converted into acetic acid and ammonia.—Distilled with phosphoric anhydride, it gives up water and is converted into acetonitrile or cyanide of methyl C^2H^3N.—Heated in a stream of dry hydrochloric acid gas, it yields a liquid and a crystalline distillate, and a brownish non-volatile residue. The liquid portion of the distillate consists of strong acetic acid, together with small quantities of chloride of acetyl, and perhaps acetonitrile. The crystalline distillate is a mixture of hydrochlorate of acetamide, and a compound of acetamide and diacetamide $C^2H^5NO.C^4H^7NO^2$; the latter compound may be extracted by ether, in which the hydrochlorate of acetamide is insoluble. The non-volatile residue consists of hydrochlorate of acediamine mixed with sal-ammoniac. The decomposition is represented by the following equations:

$$2C^2H^5NO + HCl = \underbrace{C^4H^7NO^2}_{\text{Diacetamide.}} + NH^4Cl$$

$$2C^2H^5NO + HCl = \underbrace{C^2H^6N^2.HCl}_{\text{Hydrochlorate of acediamine.}} + \underbrace{C^2H^4O^2}_{\text{Acetic acid.}}$$

$$C^2H^5NO + 2HCl = \underbrace{C^2H^3OCl}_{\text{Chloride of acetyl.}} + NH^4Cl;\ C^2H^5NO - H^2O = \underbrace{C^2H^3N.}_{\text{Acetonitrile.}}$$

Acetamide acts both as a base and as an acid, combining with hydrochloric and with nitric acid, and likewise forming salts in which 1 atom of its hydrogen is replaced by a metal.

Hydrochlorate of Acetamide, $(C^2H^5NO)^2.HCl$ is prepared :—

1. By mixing acetamide fused at a gentle heat with oxychloride of phosphorus, dissolving the resulting crystalline mass in absolute alcohol, and leaving the solution to cool, or better, mixing it with ether; hydrochlorate of acetamide is then obtained in colourless crystalline needles. The crystalline mass first produced, appears to be a compound of acetamide and oxychloride of phosphorus, and this, on addition of alcohol, yields phosphate of ethyl and hydrochloric acid, which unites with the acetamide:

$$2C^2H^5NO + POCl^3 + 3(C^2H^5.H.O) = (C^2H^5NO)^2.HCl + P(C^2H^5)^3O^4 + 2HCl.$$

2. By directing a stream of dry hydrochloric acid gas on a solution of acetamide in alcohol and ether cooled from without, washing the resulting crystalline mass with anhydrous ether, and dissolving it in warm alcohol. The solution on cooling, or more quickly on addition of ether, deposits the hydrochlorate in crystals. This mode of preparation is preferable to the former. The compound forms long spear-shaped crystals, having an acid taste and reaction, easily soluble in water and alcohol, but insoluble in ether. Heated in a sealed tube to between 180° and 200°, it decomposes, yielding the same compounds that are obtained by heating acetamide in dry hydrochloric acid gas. (Strecker, Ann. Ch. Pharm. ciii. 321.)

Nitrate of Acetamide, $C^2H^5NO.NO^3H$, is obtained by dissolving acetamide in cold strong nitric acid. It forms colourless acid crystals, which melt at a moderate heat, and detonate at a higher temperature, leaving scarcely any residue.

CHLORACETAMIDES. — *Monochloracetamide*, $C^2H^4Cl.NO = N.H^2.C^2H^2ClO$, is obtained:

1. By the action of ammonia on monochloracetate of ethyl:

$$C^2H^2ClO.C^2H^5.O + NH^3 = N.H^2.C^2H^2ClO + C^2H^6O.$$

2. By bringing perfectly dry ammoniacal gas in contact with chloride of monochloracetyl:

$$C^2H^2ClO.Cl + 2NH^3 = N.H^2.C^2H^2ClO + NH^4Cl.$$

The product is a white amorphous mass, from which absolute alcohol extracts the amide, and deposits it in large shining laminæ. The amide dissolves in 10 parts of water and 10½ parts of alcohol at 24°, but is very sparingly soluble in ether. It is decomposed by potash, yielding chloride and acetate of potassium. (E. Willm. Ann. Ch. Phys. [3] xlix. 99.)

Trichloracetamide. $C^2H^2Cl^3NO = N.H^2.C^2Cl^3O$. This compound is produced by the action of gaseous or aqueous ammonia:

1. On chloride of trichloracetyl:

$$C^2Cl^3O.Cl + 2NH^3 = N.H^2.C^2Cl^3O + NH^4Cl.$$

2. On trichloracetate of ethyl:

$$C^2Cl^3O.C^2H^5.O + NH^3 = N.H^2.C^2Cl^3O + C^2H^6O.$$

3. On chloraldehyde, C^2Cl^4O, or the polymeric compound, perchloracetic ether, $C^4Cl^8O^2$:

$$C^2Cl^4O + 2\,NH^3 = C^2H^2Cl^3NO + NH^4Cl.$$

Also by the action of ammonia on the perchlorinated ethylic ethers of formic, carbonic, oxalic, and succinic acids, all these compounds yielding chloraldehyde when heated. The best product is obtained from perchloracetic ether. The mass is treated with cold water to dissolve the sal-ammoniac, and the residual trichloracetamide is crystallised from ether. It then forms snow-white crystalline laminæ. It dissolves also in boiling water and in alcohol, and crystallises from the aqueous solution in tabular crystals belonging to the rhombic system. It has a sweetish taste; melts at 135°, begins to turn brown at 200°, and boils at about 240°. It gives off ammonia when heated with potash. Ammonia dissolves it after a while, and the solution yields, by evaporation, beautiful prisms of trichloracetate of ammonium. Anhydrous phosphoric acid converts it into chloracetonitrile or cyanide of trichloromethyl: $C^2H^2Cl^3NO - H^2O = C^2Cl^3N$. (Cloez, Ann. Ch. Phys. [3] xvii. 305; Malaguti, ibid. xvi. 5; Cahours, ibid. xix. 352; Gerhardt, Compt. chim. 1848, 277; Traité, i. 760; Gm. ix. 270.)

Tetrachloracetamide, $C^2HCl^4NO = N.H.Cl.C^2Cl^3O$; sometimes called chloracetamic acid, is formed by exposing trichloracetamide, slightly moistened with water, to the action of chorine in sunshine. It then sublimes in needles, which may be purified by crystallisation from ether. It is permanent in the air, melts when heated, and partly sublimes undecomposed. It is nearly inodorous, but has a harsh disagreeable taste. Insoluble in water, but dissolves pretty readily in alcohol and wood-spirit, and very easily in ether. It dissolves without decomposition in cold aqueous alkalis, forming crystallisable salts. When boiled with potash, it gives off ammonia, and leaves chloride and carbonate of potassium:

$$C^2HCl^4NO + 3H^2O = NH^3 + 4HCl + 2\,CO^2.$$

(Cloez, Ann. Ch. Phys. [3] xvii. 305.)

Bromacetamides and *Iodacetamides* are likewise known.

Diacetamide, $C^4H^7NO^2 = NH(C^2H^3O)^2$. The ethereal solution of the compound of acetamide and diacetamide obtained by the action of hydrochloric acid gas on acetamide, deposits, when hydrochloric acid gas is passed through it, spicular crystals of hydrochlorate of acetamide, and the liquid filtered therefrom yields by evaporation over sulphuric acid, crystals of diacetamide, easily soluble in water, alcohol, and ether. The crystals when boiled with acids are resolved into acetic acid and ammonia, but not so readily as acetamide. The alcoholic solution boiled with dichloride of platinum deposits chloroplatinate of ammonium. (Strecker.)

Ethylacetamide. See Ethylamine.

Mercuracetamide, C^2H^4HgNO. An aqueous solution of acetamide saturated with mercuric oxide deposits by evaporation in vacuo, colourless crystalline crusts sparingly soluble in alcohol. *Silver-acetamide*, C^2H^4AgNO, is obtained in a similar manner in crystalline scales.

Phenylacetamide, or Acetanilide, see Phenylamine.

ACETENE. Synonyme of Ethylene and Olefiant Gas.

ACETIC ACID. *Essigsaure, Acide Acétique.* $C^2H^4O^2 = \left.\begin{matrix}C^2H^3O\\H\end{matrix}\right\}O$, or $C^2H^3O^2.H$. The hydrate or hydrated oxide of acetyl; it may be regarded as a molecule of water (H^2O), in which half the hydrogen is replaced by acetyl C^2H^3O. (It was formerly supposed to be derived from a radicle, C^4H^3, also called acetyl, which, in combination with 3 atoms of oxygen, formed anhydrous acetic acid $C^4H^3O^3$; and this in combination with an atom of water HO, formed hydrated acetic acid, $C^4H^3O^3.HO = C^4H^4O^4$] See Acetyl.

Sources.—Acetic acid exists, in nature, in the organic kingdom only, being found in the juices of many plants, especially of trees, and existing probably also in several of the animal secretions; but more commonly it results from the decomposition and oxidation of organic bodies.

Formation.—1. By the destructive distillation of organic substances, especially of wood.—2. By the action of oxidising agents, viz. atmospheric oxygen, chromic acid nitric acid, hypochlorous acid, &c., on alcohol and other organic bodies.—3. By the action of hydrate of potassium or hydrate of sodium at a high temperature on various organic bodies, *e.g.* succinic acid, oleic acid, malic acid, sugar, alcohol, &c.—4. By heating cyanide of methyl with aqueous caustic alkalis: $CH^3.CN + 2H^2O = C^2H^4O^2 + NH^3$.—5. By the action of carbonic anhydride on sodium-methyl; $CO^2 + CH^3Na = C^2H^3NaO^2$ (acetate of sodium).—6. By the reducing action of zinc or sodium-amalgam on chloracetic acid.

Preparation.—1. From *alcohol.* Alcohol is converted into acetic acid by various processes of oxidation; *e.g.* by the action of spongy platinum. If a tray of finely-divided spongy platinum be placed on a triangle over a porcelain dish containing a little alcohol gently warmed, and the whole covered with a bell-glass standing on a wedge, and open at the top so as to allow a gentle current of atmospheric air to pass through the apparatus, the oxidation of the alcohol proceeds rapidly, acetic acid condensing in abundance on the inside of the bell-jar.

By this process, however, much of the alcohol is converted into aldehyde, and lost by volatilisation. It would appear, in fact, that, in the formation of acetic acid by direct oxidation, aldehyde is always developed as an intermediate product, especially if the oxidising influence be not sufficiently rapid—

$$\underbrace{C^2H^6O}_{\text{Alcohol.}} + O = \underbrace{C^2H^4O}_{\text{Aldehyde.}} + H^2O;\ \text{and}\ \underbrace{C^2H^4O}_{\text{Aldehyde.}} + O = \underbrace{C^2H^4O^2}_{\text{Acetic acid.}}$$

The oxidation of alcohol by atmospheric oxygen is greatly promoted by the presence of ferments; and, in fact, in the ordinary processes for making vinegar, an alcoholic solution is exposed to the joint influence of air and a ferment. In France and Germany wine is usually employed, and in England malt.

Wine Vinegar (*Weinessig, Vinaigre*).—The following is the plan of making vinegar practised in Paris. The wine destined for vinegar is mixed in a large tun with a quantity of wine-lees, and the whole being transferred into cloth-sacks, placed within a large iron-bound vat, the liquid matter is squeezed through the sacks by superincumbent pressure. What passes through is put into large casks set upright and having a small aperture at the top. In these it is exposed to the heat of the sun in summer, or to that of a stove in winter. Fermentation supervenes in a few days. If the heat should then rise too high, it is lowered by cool air and the addition of fresh wine. In the skilful regulation of the fermentative temperature consists the art of making good wine-vinegar. In summer, the process is generally completed in a fortnight; in winter, double the time is requisite. The most favourable temperature is between 25° and 30° (77° and 86° F.). The vinegar is then run off into barrels containing several chips of birch wood. In about a fortnight it is found to be clarified, and is then fit for the market. It must be kept in close casks.

At the same time that the alcohol is thus acidified, the nitrogenous organic matters which have served as ferments have likewise assumed new forms, and settled at the bottom of the vessel in the form of a white gelatinous mass, known as "mother of vinegar." This substance, which has been described by Mulder as a fungoïd plant, under the name of *Mycoderma Vini*, is a nitrogenised body, which has the power of exciting the acetification of pure alcohol in the presence of atmospheric air, probably in consequence of its own tendency to change. By treating it with potash, the whole of the nitrogen is removed, pure cellulose alone remaining.

A slight motion is found to favour the formation of vinegar, and to endanger its decomposition after it is made. Chaptal ascribes to agitation the operation of thunder, though it is well known, that when the atmosphere is highly electrified, beer is apt to become suddenly sour, without the concussion of a thunder-storm. Vinegar does not keep well in cellars exposed to the vibrations occasioned by the rattling of carriages. The lees, which had been deposited by means of isinglass during repose, are thus jumbled into the liquor, and promote the fermentation.

Almost all the vinegar of the north of France being prepared at Orleans, the manufacture of that place has acquired such celebrity as to render the process worthy of a separate consideration.

The Orleans casks contain nearly 400 pints of wine. Those which have been already used are preferred. They are placed in three rows, one over another, the upper ones having an aperture of two inches diameter, kept always open. The wine for acetification is kept in adjoining casks containing beech shavings, to which the lees adhere. The wine thus clarified is drawn off to make vinegar. One hundred pints of good vinegar, boiling hot, are first poured into each cask, and left there for eight days; ten pints of wine are mixed in, every eight days, till the vessels are full; and the vinegar is allowed to remain in this state fifteen days, before it is exposed for sale. The manufacturers at Orleans prefer wine of a year old for making vinegar; but if the wine has lost its extractive matter by age, it does not readily undergo the acetous fermentation.

The *used* casks, called *mothers*, are never emptied more than half, but are successively filled again, to acetify new portions of wine. In order to judge if the *mother* works, the vinegar makers plunge a spatula into the liquid; and according to the quantity of froth which the spatula shows, they add more or less wine. In summer, the atmospheric heat is sufficient. In winter, stoves heated to about 76° Fahr. maintain the requisite temperature in the manufactory.

Quick method of Vinegar-making (*Schnellessigbereitung*). Since the efficient conversion of the alcohol into acetic acid essentially depends upon the completeness of the oxidation, the German chemists have proposed to promote this result by enlarging the surface of the liquid exposed to the air. This is effected by allowing the alcoholic liquor to trickle down in a fine shower from a colander through a large oaken tube (called the vinegar generator, or graduator), filled with beech chips, up which a current of air ascends through apertures in the sides. By the oxidation which goes on, the temperature of the liquid rises to 37° or 40° C. (100 or 104° Fahr.). The liquid requires to be passed three or four times through the cask before the acetification is complete, which takes place in twenty-four or thirty-six hours. Care should be taken to allow a sufficient supply of air.

In England the same result is often attained by causing the alcoholic liquor to be distributed by means of a Barker's mill or other contrivance, over the beech shavings in a tun, whilst a current of air is forced up through it by two floating gasometers which are made to rise and fall alternately by steam power.

Wine vinegar is of two kinds, white or red, according as it is prepared from white or red wine. It contains, besides acetic acid and water, sugar, colouring matter, gum, and salts, especially bitartrate of potassium. Its specific gravity varies from 1·014 to 1·022.

MALT VINEGAR.—This is prepared from malt or a mixture of malt and raw barley, which is mashed with water as in the ordinary operation of brewing; the wort is then submitted to the vinous fermentation and the liquor thus obtained is converted by oxidation into vinegar. This effected in two ways; either by the process of *fielding* or *stoving*.

When *fielding*, that is, exposure to the open air, is resorted to, the wort must be made in the spring months, and then left to finish during several months of the warm season. In consequence, therefore, of the length of time required, the latter, or *stoving* process, is more generally used. The wash is introduced into barrels standing endways, tied over with a coarse cloth, and placed close together in darkened chambers, artificially heated by a stove. The liquor remains in these barrels until the acetification is complete. This usually occupies several weeks or months. The product is next introduced into large tuns with false bottoms, on which *rape* (the residuary fruit from the making of British wines) is placed, and allowed slowly to filter through them. Below the false bottom and above the true one is placed a tap which allows the vinegar to flow into a back or cistern. From this cistern a pump raises the liquid to the top of the vessel, and thence it flows through the rape to be again returned. Or sometimes the rape tuns are worked by pairs, one of them being quite filled with vinegar from the barrels, the other only three parts, so that the acetification is excited more readily in the latter than the former, and every day a portion of the vinegar is conveyed from one to the other, till the whole is finished and fit for sale.

Malt vinegar has a yellowish red colour, an agreeable acid taste, which is due to acetic acid; but the aromatic odour which distinguishes both it, and also wine vinegar, from pyroligneous acid (to be afterwards described) is imparted to it by the presence of acetic and other ethers.

Vinegar of four different strengths is sold by the makers, distinguished as Nos. 18, 20, 22, and 24. The last, which is the strongest, and is called proof vinegar, contains 5 per cent. of real acetic acid; its specific gravity is 1·019. (Pereira.)

Vinegar is liable to undergo a putrefactive decomposition, which was believed by the makers to be prevented by the addition of sulphuric acid, and they are allowed by law to add one-thousandth part by weight of sulphuric acid. It is now known that this is unnecessary; nevertheless the practice is still continued.

Distilled Vinegar.—By submitting wine or malt vinegar to distillation it is deprived of its colouring and other non-volatile matters, a colourless limpid liquid being obtained which is known in commerce as distilled vinegar. The product is, however, always weaker than the vinegar from which it has been derived, because the boiling point of strong acetic acid is above that of water; it is also liable to be contaminated with a small quantity of alcohol and empyreumatic bodies.

2. From *Wood*. Wood Vinegar, or Pyroligneous Acid.—The greater part of the acetic acid now employed in the arts is obtained by the destructive distillation of wood. The wood is heated in large iron cylinders like gas retorts, connected with a series of condensing vessels, the uncondensable gases which are evolved in large quantity being conveyed by pipes into the fire and aiding to maintain the heat. The liquid which condenses in the receivers consists of water, tar, wood-spirit or methylic alcohol, acetate of methyl, and acetic acid. The watery liquid, after being separated from the tar, is redistilled, the wood-spirit passing over among the first portions of the distillate, and the acetic or pyroligneous acid afterwards. The acid thus obtained is coloured, and has a strong tarry flavour, which cannot be removed by redistillation. To purify this crude acid, it is converted into acetate of sodium, either by direct saturation with carbonate of sodium, or more economically by saturating it with carbonate of calcium, and decomposing the calcium-salt with sulphate of sodium; and the acetate of sodium is purified from tarry matter, first by gentle torrefaction, and afterwards by recrystallisation. It is then decomposed by strong sulphuric acid diluted with half its weight of water, whereupon the sulphate of sodium, being insoluble in acetic acid, separates in the crystalline form, and may be separated by simple decantation; and the acetic acid thus separated is purified from the last traces of sulphate of sodium by distillation.

The process just described yields a very pure acid, but it is too expensive, principally in consequence of the large quantity of fuel which it requires. A more economical process has been proposed by Völckel (Ann. Ch. Pharm. lxxxii. 49; Chem. Soc. Qu. J. v. 274). In this process the crude wood-vinegar is immediately saturated with lime, without previous rectification. Part of the tarry matter then separates in combination with the lime, while the rest remains in solution with the acetate of calcium. The liquid, after being clarified by repose, or by filtration, is evaporated down to half its bulk in an iron pot, and mixed with a quantity of hydrochloric acid, sufficient to give it a slight acid reaction. The greater part of the tarry matter then separates, and may be skimmed off from the surface. The hydrochloric acid also decomposes certain compounds of the lime with creosote and other volatile substances, which are then expelled by heat; 33 gallons of crude wood-vinegar require for purification from 4 to 5 lbs. of hydrochloric acid. The acetate of calcium thus purified is completely dried and distilled with hydrochloric acid, 100 parts of the dry salt requiring from 90 to 95 parts of hydrochloric acid of sp. gr. 1·15 (or 20° Bm.). The sp. gr. of the acetic acid thus obtained is about 1·06 (8° Bm.). If it contains hydrochloric acid, it may be purified by redistillation, with addition of a small quantity of carbonate of sodium, or better, 2 or 3 per cent. of bichromate of potassium, which, at the same time, destroys certain organic impurities that impart a peculiar odour to the acid.

The presence of hydrochloric or sulphuric acid in vinegar is easily detected by boiling the liquid for about twenty minutes with a small quantity of potato-starch, then leaving it to cool and adding a few drops of iodide of potassium. If the vinegar is pure, the blue colour of iodide of starch immediately makes its appearance, but not if sulphuric or hydrochloric acid is present, because these acids boiled with starch convert it into dextrin, which is not coloured blue by iodine (Payen). Sulphuric acid may also be detected by chloride of barium, and hydrochloric acid by nitrate of silver.

[For further details of the manufacture of acetic acid, see the new edition of *Ure's Dictionary of Arts, Manufactures and Mines*, vol. i. pp. 5 to 20.]

CRYSTALLISABLE OR GLACIAL ACETIC ACID.—This term is applied to the pure acid $C^2H^4O^2$, [or $C^4H^4O^4$] of sp. gr. 1·0635, because it is at ordinary temperatures a crystalline solid. The acid obtained by either of the processes above described consists of this compound more or less mixed with water. On distilling this dilute acid, a weaker acid passes over, and a stronger acid remains behind, because the boiling point of aqueous acetic acid increases with its concentration; and by repeated fractional distillation, an acid is at length obtained which crystallises at a low temperature. Crystallisable acetic acid is, however, more conveniently obtained by distilling certain acetates in the dry state with an equivalent quantity of concentrated sulphuric acid or disulphate of potassium; thus with acetate of potassium:

$$2C^2H^3KO^2 + SO^4H^2 = 2C^2H^4O^2 + SO^4K^2.$$

and:

$$C^2H^3KO^2 + SO^4HK = C^2H^4O^2 + SO^4K^2.$$

The proportions required are 98 pts. of dry acetate of potassium, or 82 acetate of sodium, or 79 acetate of calcium, or 163 acetate of lead, to 49 parts of monohydrated sulphuric acid, SO^4H^2, or 136 parts of disulphate of potassium, SO^4HK. Glacial acetic acid may also be conveniently obtained from diacetate of potassium, $C^2H^3KO^2.C^2H^4O^2$ by simple distillation. When neutral acetate of potassium is mixed with aqueous acetic acid, not too dilute, and distilled, part of the acetic acid unites with the neutral acetate, and a weaker acid passes over. But as the distillation goes on, the acid potassium-salt decomposes, the distillate becomes continually richer in acetic acid, and at length the pure crystallisable acid distils over. The temperature must not be allowed to exceed 300°; otherwise the acid suffers partial decomposition, and becomes coloured (Melsens, Compt. rend. xix. 611).—Crystallised acetate of copper also yields glacial acetic acid, when dried at a temperature between 160° and 180° and afterwards distilled at a higher temperature. Towards the end of the distillation the acid becomes mixed with acetone: that which passes over towards the middle must be redistilled to free it from copper mechanically carried over, probably in the form of cuprous acetate. The acid obtained by this process was formerly called *Spiritus Aeruginis* or *Spiritus Veneris*.

Properties.—Pure acetic acid solidifies at or below 15° C. in prismatic or tabular crystals. In closed vessels it remains liquid at 12°, and does not solidify till the vessel is opened and shaken. Its specific gravity in the solid state is 1·100 at 8·5 (Persoz). It melts at 16° (Lowitz), at or above 22°·5 (Mollerat), forming a thin colourless liquid of sp. gr. 1·063 (Mollerat); 1·065 at 13° (Persoz); 1·0635 at 15° (Mohr); 1·0622 (Sébille-Auger); 1·08005 reduced to 0° (Kopp, Pogg. Ann. lxxii. 1). It boils at 119° (Sébille-Auger); at 117°·3 (Kopp). The density of its vapour is different at different temperatures, compared with an equal bulk of air at the same temperature. At temperatures considerably above the boiling point, it follows the ordinary law of condensation to 2 volumes; thus at 300° and upwards the sp. gr. of the vapour is found by Cahours to be 2·00, which agrees almost exactly with the calculated density, supposing the molecule to occupy 2 volumes. For the atomic weight of acetic acid, compared with hydrogen as unity is 60 ($= 2C + 4H + 2O = 24 + 4 + 32$); and if this be the weight of 2 volumes of the vapour, it follows that the weight of 1 volume of vapour, or in other words, the specific gravity as compared with hydrogen, will be 30; and multiplying this number by 0·0693, the sp. gr. of hydrogen referred to air as unity, we obtain for the sp. gr. of acetic acid vapour referred to air as unity, the number 2·079.

But at temperatures near the boiling point, the density of the vapour is much greater, exhibiting a condensation to $\frac{3}{2}$-volume, or even less. The following table exhibits the density of the vapour at various temperatures as determined by Cahours (Compt. rend. xix. 771; xx. 51):

Temperature.	125°	130°	140°	150°	160°	170°	190°	200°	230°	250°	300°
Density.	3·20	3·12	2·90	2·75	2·48	2·42	2·30	2·22	2·17	2·09	2·08

The tension of the vapour is 7 mm. at 15°; 14·5 mm. at 22°, and 32 mm. at 32°. (Bineau, Ann. Ch. Phys. [3] xviii. 226.)

The acid has a pungent sour taste and odour, blisters the skin, and acts as an acrid poison. It does not redden litmus paper *per se*, but very strongly when mixed with water.

Decompositions.—1. The vapour of acetic acid is inflammable, and burns with a blue flame, producing water and carbonic acid. When it is passed through a red-hot tube, the greater part remains unaltered, but a portion is decomposed, yielding free carbon and combustible gases, together with acetone, napthalin, hydrate of phenyl and benzol. (Berthelot, Ann. Ch. Phys. [3] xxxiii. 295.)

2. A mixture of glacial acetic and strong *sulphuric acid* blackens when heated, giving off carbonic and sulphurous anhydrides. *Fuming sulphuric acid* mixes with glacial acetic acid without evolution of gas; but the mixture becomes hot, and if it be raised to a higher temperature, carbonic anhydride is given off, mixed with only a small quantity of sulphurous anhydride. *Sulphuric anhydride* dissolves in acetic acid without evolution of gas, and on heating the mixture, sulphacetic acid is produced.

3. Acetic acid is not sensibly attacked by *nitric acid.*

4. *Periodic acid* converts it into carbonic or formic acid, with formation of iodic acid and separation of iodine.

5. *Chlorine* in sunshine converts acetic acid into monochloracetic and trichloracetic acids, the quantity of the one or the other being greater, according as the acetic acid or the chlorine is in excess. See CHLORACETIC ACID.

6. Glacial acetic acid heated with *bromine* in a sealed tube forms bromacetic and dibromacetic acids. *Iodine* has no action on acetic acid even in sunshine.

7. With *pentachloride of phosphorus*, glacial acetic acid forms hydrochloric acid, chloride of acetyl and oxychloride of phosphorus:

$$C^2H^3O.H.O + PCl^3.Cl^2 = C^2H^3O.Cl + HCl + PO.Cl^3.$$

8. With *pentasulphide of phosphorus*, it forms thiacetic acid and phosphoric anhydride:

$$5(C^2H^3O.H.O) + P^2S^5 = P^2O^5 + 5(C^2H^3O.H.S).$$

The difference between the mode of action of the pentachloride and pentasulphide of phosphorus, the former giving rise to two distinct chlorine-compounds, $C^2H^3O.Cl$ and HCl, whereas the latter forms only one sulphur-compound, is very remarkable, and shows clearly the propriety of regarding chlorine as a monatomic, and sulphur as a diatomic radicle.

AQUEOUS ACETIC ACID.—Acetic acid mixes with water in all proportions, imparting to it its taste and smell. The density of the aqueous acid varies with its strength in a remarkable manner. When water is gradually added to glacial acetic acid, the density increases till a hydrate is formed containing 79 pts. of crystallised acid to 21 water, and having the composition $C^2H^4O^2.\ H^2O$. This hydrated acid has a density of 1·073 and boils at 104°. All further additions of water diminish the density of the acid.

The following table constructed by Mohr (Ann. Ch. Pharm. xxxi. 277) gives the quantity of crystallisable acetic acid in 100 pts. of the aqueous acid of different densities.

Perc.	Sp. Gr.	Perc.	Sp. Gr.	Perc.	Sp. Gr.	Perc.	Sp. Gr.	Perc.	Sp. Gr.
100	1·0635	80	1·0735	60	1·067	40	1·051	20	1·027
99	1·0655	79	1·0735	59	1·066	39	1·050	19	1·026
98	1·0670	78	1·0732	58	1·066	38	1·049	18	1·025
97	1·0680	77	1·0732	57	1·065	37	1·048	17	1·024
96	1·0690	76	1·0730	56	1·064	36	1·047	16	1·023
95	1·0700	75	1·0720	55	1·064	35	1·046	15	1·022
94	1·0706	74	1·0720	54	1·063	34	1·045	14	1·020
93	1·0708	73	1·0720	53	1·063	33	1·044	13	1·018
92	1·0716	72	1·0710	52	1·062	32	1·042	12	1·017
91	1·0721	71	1·0710	51	1·061	31	1·041	11	1·016
90	1·0730	70	1·0700	50	1·060	30	1·040	10	1·015
89	1·0730	69	1·0700	49	1·059	29	1·039	9	1·013
88	1·0730	68	1·0700	48	1·058	28	1·038	8	1·012
87	1·0730	67	1·0690	47	1·056	27	1·036	7	1·010
86	1·0730	66	1·0690	46	1·055	26	1·035	6	1·008
85	1·0730	65	1·0680	45	1·055	25	1·034	5	1·007
84	1·0730	64	1·0680	44	1·054	24	1·033	4	1·005
83	1·0730	63	1·0680	43	1·053	23	1·032	3	1·004
82	1·0730	62	1·0670	42	1·052	22	1·031	2	1·002
81	1·0732	61	1·0670	41	1·051	21	1·029	1	1·001

Mollerat, Ann. Chim. lxviii. 88, and **Ad. van Toorn** (J. pr. Chem. vi. 171) have also given tables of the specific gravities of acetic acid of different degrees of concentration.

It will be seen from the preceding table that the specific gravity of acetic acid varies but slowly, a difference of 1 per cent. corresponding to a difference of only ·001 in the density, and sometimes even less. For this reason, the determination of the strength of commercial acetic acid by the hydrometer or *acetometer*, as it is called when graduated for this purpose, is not much to be depended on. The presence of colouring matter, saline substances and other impurities, which frequently occur in vinegar, are of course an additional source of inaccuracy in this method of estimation. It is better, therefore, to determine the strength of the acid by ascertaining the quantity of a standard solution of caustic soda or ammonia, required to neutralise a given volume. (See ACIDIMETRY and ANALYSIS, VOLUMETRIC.) This method, when applied to acetic acid, is affected with a slight source of inaccuracy, arising from the fact that the normal or neutral acetates of the alkalis exhibit a slight alkaline reaction. The error thence arising is, however, of small amount, not exceeding $\frac{1}{10}$ per cent. for an acid containing 10 per cent. of crystallisable acetic acid, as shown by **Otto** (Ann. Ch. Pharm. cii. 69). Moreover, it may be completely obviated by using a solution of caustic soda, graduated for the purpose by means of a solution of pure acetic acid of known strength (ANALYSIS, VOLUMETRIC). **Greville Williams** (Pharm. J. Trans. xiii. 594) recommends for the volumetric estimation of acetic acid a graduated solution of lime in sugar-water.

Acetic acid mixes in all proportions with alcohol. It dissolves resins, gum-resins, camphor, and essential oils. Its use for culinary purposes is well known. Its odour is employed in medicine to relieve nervous head-ache, fainting fits, or sickness occasioned by crowded rooms. Pungent smelling salts consist of sulphate of potassium moistened with glacial acetic acid. Pyroligneous acid is largely used in calico-printing; the tar and empyreumatic substances present in it appear to be rather advantageous than otherwise for that purpose. Large quantities of acetic acid are also used for the preparation of the acetates of lead, copper, aluminium, &c. (See *Dictionary of Arts, Manufactures, and Mines.*)

Acetates.—Acetic acid is monobasic, the general formula of its normal salts being $C^2H^3O^2.M$ [or $C^4H^3O^4.M = C^4H^3O^3.MO$], the symbol M denoting a metal. It also forms basic salts, which may be regarded as compounds of the normal acetates with oxides. The normal acetates all dissolve in water, and most of them readily. The least soluble are the silver and mercury salts, so that solutions of other acetates added to mercurous nitrate or nitrate of silver, throw down white shining scales of mercurous acetate or silver-acetate; but generally speaking, acetates are not formed by precipitation: they are produced by the action of acetic acid on metallic oxides or carbonates; many carbonates, however, the barium and calcium salts, for example, are not decomposed by acetic acid in its most concentrated state, but only after addition of water.

All acetates are decomposed by heat, most of them yielding carbonic anhydride, acetone and an empyreumatic oil. Those which are easily decomposed, and likewise contain bases forming stable carbonates, are almost wholly resolved into acetone and a carbonate of the base; this is especially the case with acetate of barium:

$$2C^2H^3O^2Ba = C^3H^6O + CO^3Ba^2.$$

Those which, like the potassium and sodium salts, require a higher temperature to decompose them, yield more complex products, but always a certain quantity of acetone. Among the products are found certain homologues of acetone, viz. *methylacetone* $C^3H^5(CH^3)O$ and *ethylacetone* $C^3H^5(C^2H^5)O$, together with *dumasin* $C^6H^{10}O$. (**Fittig**, Ann. Ch. Pharm. cx. 17). Acetates containing weaker bases, give off part of the acetic acid undecomposed, the remaining portion being resolved into acetone and carbonic anhydride, or if the heat be strong, yielding empyreumatic oil and charcoal: the residue consists sometimes of oxide, sometimes, as in the case of copper and silver, of reduced metal; in this case part of the acetic acid is burnt by the oxygen abstracted from the metal. Acetates heated with a large excess of fixed caustic alkali, are resolved at a temperature below redness into marsh gas and alkaline carbonate, *e. g.*:

$$C^2H^3KO^2 + KHO = CH^4 + CO^3K^2.$$

Acetates distilled with sulphuric acid, give off the odour of acetic acid, and yield a distillate which dissolves oxide of lead, and acquires thereby an alkaline reaction. Distilled with sulphuric and alcohol, they yield acetate of ethyl, recognisable by its odour. The neutral acetates impart to solutions of ferric salts a reddish yellow or red-brown colour, according to the degree of dilution. Acetates heated to redness with arsenious acid give off the odour of cacodyl. The acetates of the alkali-metals, and probably others also, treated with oxychloride of phosphorus, yield chloride of acetyl, together with a tribasic phosphate:

$$3(C^2H^3O.Na.O) + PO.Cl^3 = 3C^2H^3OCl + PO^4Na^3.$$

ACETATES OF ALUMINIUM. — *a. Triacetate.* As aluminium is sesquiatomic (Al^2 being equivalent to H^6 or $Al^{\frac{2}{3}}$ to H) the normal salt should be a triacetate $C^2H^3O^2.Al^{\frac{2}{3}}$ or $(C^2H^3O^2)^6.Al^2$, [or $Al^2O^3.3C^4H^3O^3$, regarding it as a compound of alumina with anhydrous acetic acid]. This salt, however, exists only in solution, and is decomposed by evaporation. The solution is obtained by digesting recently precipitated trihydrate of aluminium in strong acetic acid, or by precipitating a solution of the trisulphate with acetate of lead:

$$(SO^4)^6Al^4 + 6C^2H^3O^2Pb = 3SO^4Pb^2 + 2(C^2H^3O^2)^6Al^2.$$

This salt is largely used as a mordant in dyeing and calico-printing, and is generally prepared for this purpose by precipitating alum with acetate of lead. The solution thus formed contains sulphate of potassium as well as acetate of aluminium.

β. Diacetate. When the solution of the triacetate obtained by decomposing trisulphate of aluminium with acetate of lead is evaporated at a low temperature, with sufficient rapidity, as by spreading the concentrated liquid very thinly on plates of glass or porcelain, exposing it to a temperature not exceeding 100° F. (37°·7 C.), and, as it runs together in drops, rubbing it constantly with a spatula, *diacetate of aluminium* remains in the form of a dry powder containing $\left.\begin{matrix}(C^2H^3O)^2\\Al^4\end{matrix}\right\}O^4 + 5H^2O$ [or, using the smaller atomic weights of carbon and oxygen, $2C^4H^3O^3.Al^2O^3 + 5HO$]. The diacetate thus obtained dissolves easily and completely in water, and the solution when heated deposits dihydrate of aluminium soluble in water. (See ALUMINIUM.) But when the solution, instead of being quickly evaporated, is left to itself in the cold for some days, it deposits a white saline crust, which is an *allotropic diacetate of aluminium insoluble in water.* Heat effects the same change more rapidly, and the insoluble diacetate then separates in the form of a granular powder. At the boiling temperature, the liquid is thus deprived in half an hour of the whole of its alumina, which goes down with ⅔ of the acetic acid, leaving ⅓ in the liquid. The insoluble diacetate digested in a large quantity of water is gradually changed into the soluble modification, part of which is, however, decomposed during the process into acetic acid and the soluble dihydrate. (Walter Crum, Chem. Soc. Qu. J. vi. 217.)

ACETATES OF AMMONIUM. — *a. Normal acetate.* $C^2H^3O^2.NH^4$. A white odourless salt, obtained by saturating glacial acetic acid with dry ammonia. It is very difficult to obtain it in the crystalline form: for its aqueous solution loses ammonia on evaporation, and is converted into the acid salt (β). It is readily soluble in water and alcohol. Its aqueous solution, known in the Pharmacopeia as *Spiritus Mindereri*, is prepared by saturating aqueous acetic acid with ammonia or carbonate of ammonium. This solution is transparent and colourless, with a peculiar odour and cooling pungent taste. When kept it is decomposed, and becomes alkaline, owing to the formation of carbonate of ammonium; by heat it is converted into a solution of the acid salt (β).

β. Acid Acetate, $C^2H^3O^2.NH^4.C^2H^4O^2$ [or $C^4H^3O^3.NH^4O + C^4H^3O^3.HO$]. Obtained as a white crystalline sublimate when dry powdered chloride of ammonium is heated with an equal weight of acetate of potassium or calcium, ammonia being given off simultaneously. A warm saturated solution of this salt, kept in a closed bottle deposits long needle-shaped crystals. This salt is also obtained in a radiated crystalline mass, by evaporating the aqueous solution of the normal salt (*a*). The crystals redden litmus and deliquesce rapidly in the air. They melt at 76°C. and sublime undecomposed at 121°. The composition of this salt is probably that expressed by the above formula.

ACETATE OF BARIUM, $C^2H^3O^2 Ba$.—Prepared by decomposing carbonate or sulphide of barium with acetic acid. The solution evaporated at a gentle heat yields flattened prisms containing $2C^2H^3O^2Ba + H^2O$, but when cooled to 0° C. it yields rhomboidal prisms, isomorphous with acetate of lead, and containing $2C^2H^3O^2Ba + 3H^2O$. The crystals dried at 0° yield the anhydrous salt in the form of a white powder, which, when strongly heated, is resolved into acetone and carbonate of barium.

ACETATE OF BISMUTH separates in micaceous laminæ from a warm mixture of nitrate of bismuth and acetate of potassium. Acetic acid mixed with a solution of nitrate of bismuth prevents the precipitation of a basic salt of that metal by water.

ACETATE OF CADMIUM.—Small prismatic crystals very soluble in water (Stromeyer). According to Meissner and John, it is not crystallisable, but forms a gelatinous mass.

ACETATE OF CALCIUM, $C^2H^3O^2Ca$, crystallises in prismatic needles, which effloresce in the air, and dissolve in water and in alcohol. The salt is decomposed by heat into acetone and carbonate of calcium. A solution of acetate and chloride of calcium in equivalent proportions yields by slow evaporation, large crystals containing $C^2H^3O^2Ca.ClCa + 5H^2O$.

ACETATE OF CERIUM.—Small needles sparingly soluble in alcohol.

Acetates of Chromium.—The *chromous salt*, $2C^2H^3O^2Cr + H^2O$ is, produced by pouring protochloride of chromium into a solution of acetate of potassium or sodium. It forms red transparent crystals, which when moist absorb oxygen very rapidly from the air, undergoing a true combustion. The *chromic* salt is obtained as a green crystalline crust, very soluble in water, by dissolving chromic hydrate in acetic acid: the solution scarcely reddens litmus.

Acetates of Cobalt.—The red liquid formed by dissolving carbonate of cobalt in acetic acid, yields by evaporation a red residue which turns blue when heated. It may be used as a sympathetic ink. The oxides Co^4O^3 and Co^3O^2 also dissolve in acetic acid without separation of oxygen, forming brown solutions. The solution of the sesquioxide sustains a boiling heat without decomposition.

Acetates of Copper.—*a. Cuprous Acetate*, $C^2H^3O^2Ccu$. [$Ccu = Cu^2 = 63{\cdot}2$]. This salt sublimes towards the end of the distillation of normal cupric acetate. According to Berzelius, it is contained in common green verdigris, and sublimes when that substance is distilled. It forms soft, loose, white flakes, which redden litmus and have a caustic astringent taste. Water decomposes it into normal cupric acetate and yellow cuprous hydrate.

b. Cupric Acetates.—(Berzelius, Pogg. Ann. ii. 233; Traité, iv. 173; Gm. viii. 323; Gerh. i. 728.) Four of these salts are known, viz.:—

Normal Cupric Acetate	$C^2H^3O^2Cu$		$= C^4H^3O^3 \,.\, CuO.$
Sesquibasic . . .	$(C^2H^3O^2Cu)^4$	$. Cu^2O$	$= (C^4H^3O^3)^2 \,.\, (CuO)^3.$
Dibasic . . .	$(C^2H^3O^2Cu)^2$	$. Cu^2O$	$= C^4H^3O^3 \,.\, (CuO)^2.$
Tribasic . . .	$C^2H^3O^2Cu$	$. Cu^2O$	$= C^4H^3O^3 \,.\, (CuO)^3.$

1. The normal salt $C^2H^3O^2Cu$, called also *Crystallised Verdigris, Verdet, Cristaux de Venus*, is produced by dissolving cupric oxide or common verdigris in acetic acid, or by precipitating a solution of normal acetate of lead with sulphate of copper: in either case, the liquid must be highly concentrated and then left in a cool place. It forms dark bluish-green prisms belonging to the monoclinic system, and containing $2C^2H^3O^2Cu + H^2O$. The ordinary combination is $\infty P \,.\, 0P \,.\, +P \,.\, +2P\infty$. Twin-crystals also occur. Ratio of the axes: $a : b : c = 0{\cdot}6473 \; 1 : 0{\cdot}5275$. Inclination of the axes = 63°. Inclination of the faces, $\infty P : \infty P$ in the plane of the orthodiagonal and the principal axis = 108°; $\infty P : 0P = 105° \, 30'$; $0P : +2P\infty = 119° \, 4'$. Cleavage parallel to $0P$ and ∞P. The salt is efflorescent, soluble in water, sparingly soluble in alcohol, and poisonous like all soluble copper-salts. The crystals after drying in vacuo at ordinary temperatures, suffer no further diminution in weight at 100°, but give off 9·6 per cent. of water between 110° and 140°, then nothing more below 240°; between 240° and 260° strong acetic acid, which when rectified yields 32 per cent. of the crystallisable acid; at 270° white fumes which condense into white flakes of cuprous acetate; and lastly a mixture of carbonic anhydride and a combustible gas. At 330° the decomposition is complete, and a reddish substance remains consisting chiefly of metallic copper. The solution boiled with sugar yields a red precipitate of cuprous oxide. Acetate of copper crystallised at a temperature near 8°, yields crystals containing $2C^2H^3O^2Cu + 5H^2O$.

2. The basic cupric acetates are contained in *common verdigris* (*vert-de-gris, Grünspan*), a substance obtained by exposing plates of copper to the air in contact with acetic acid, and much used as a pigment and as a mordant in dyeing wool black. There are two varieties of this substance, the blue and the green, the former consisting almost wholly of dibasic cupric acetate, the latter of the sesquibasic salt mixed with smaller quantities of the dibasic and tribasic acetates. The *dibasic salt* or *blue verdigris* is prepared at Montpellier and in other parts of the south of France, by exposing copper to the air in contact with fermenting wine-lees. The wine-lees are loosely packed in casks together with straw, till they pass into the state of acetous fermentation; and when that is ended, they are arranged in pots covered with straw, in alternate layers with rectangular plates of copper, which when used for the first time, are previously moistened with a cloth dipped in a solution of normal acetate of copper, and then dried. At the end of three weeks, the plates are taken out; placed in an upright position to dry; dipped six or eight times in water in the course of as many weeks; and again left to dry, during which operations the verdigris continually swells up. It is then scraped off, the plates again arranged alternately with sour wine-lees, and the same processes are repeated till the plates are quite corroded. The same compound is obtained by exposing copper plates to damp air in contact with normal acetate of copper made into a paste with water. It forms delicate, silky, blue, crystalline needles and scales, which yield a beautiful blue powder. They contain 6 at. water, which they give off at 60°, and are then converted into a green mixture of the monobasic and tribasic salt:—

$$(C^2H^3O^2Cu)^2.Cu^2O = C^2H^3O^2Cu + C^2H^3O^2Cu \,.\, Cu^2O.$$

By repeated exhaustion with water, it is resolved into the insoluble tribasic salt, and a solution of the normal and sesquibasic salts:

$$5(C^4H^6O^3.2Cu^2O) = 2(C^4H^6O^3.3Cu^2O) + 2C^4H^6O^3.3Cu^2O + C^4H^6O^3.Cu^2O.$$

The following table exhibits the composition of several kinds of blue verdigris as determined by Berzelius and by Phillips:

				Phillips.		
				French.	English.	
Calculation.			Berzelius.		Crystallised.	Compressed.
$2Cu^2O$	160	43·24	43·34	43·5	43·25	44·25
$C^4H^6O^3$	102	27·57	27·45	29·3	28·30	29·62
$6H^2O$	108	29·19	29·21	25·2	28·45	25·51
Impurities	..	..	..	2·0	..	0·62
	370	100·00	100·00	100·0	100·00	100·00

The *sesquibasic acetate* is obtained in a state of purity by adding ammonia in small portions to a boiling concentrated solution of the normal salt, till the precipitate is just redissolved, and leaving the solution to cool; or by treating common green verdigris with cold or tepid water, and leaving the filtrate to evaporate. It is then deposited in bluish scales containing $(C^2H^3O^2Cu)^4. Cu^2O + 6H^2O$. It gives off half its water at 60°, and becomes greenish.

Green Verdigris, according to Berzelius, is a mixture of this salt with small quantities of the dibasic and tribasic salts, sometimes also containing cuprous acetate and other impurities. It is manufactured at Grenoble by frequently sprinkling copper-plates with vinegar in a warm room; and in Sweden by disposing copper-plates in alternate layers with flannel cloths soaked in vinegar, till the green salt begins to form, then exposing them to the air and frequently moistening with water. The greenest kind contains according to Berzelius, 49·9 per cent. of cupric oxide, and 13·5 per cent. of water and impurities; the pure sesquibasic salt contains 43·5 per cent. Cu^2O.

The *tribasic acetate*, $C^2H^3O^2Cu.Cu^2O + H^2O$, is the most stable of all the acetates of copper. It is obtained by exhausting blue verdigris with water; also by boiling the aqueous solution of the normal salt, or by heating it with alcohol, or again by digesting the same solution with cupric hydrate. The last method yields the salt in the form of a green powder; as obtained by the other methods, it forms a bluish powder composed of fine needles or scales. It gives off its water at 160°, and decomposes at a higher temperature, yielding acetic acid. Boiling water decomposes and turns it brown. The brown substance thus formed was regarded by Berzelius as a peculiar basic acetate, containing $C^4H^6O^3. 48Cu^2O$; but it is more probably a mixture of the tribasic salt with excess of oxide.

Acetate of Copper and Calcium. $C^2H^3O^2Ca . C^2H^3O^2Cu + 4H^2O$.—Obtained by heating a mixture 1 atom of normal cupric acetate and 1 atom hydrate of calcium with 8 times its weight of water and sufficient acetic acid to dissolve the precipitated oxide of copper, and evaporating the green filtrate at a temperature between 25° and 27°. It forms large, blue, transparent, square prisms, often converted into octagonal prisms by truncation of the lateral edges. They effloresce slightly in the air; fall to powder at 75°, giving off acetic acid; and dissolve readily in water. Another cuprico-calcic acetate, $C^2H^3O^2Ca + (C^2H^3O^2Cu). Cu^2O + 2H^2O$, often exists in crystallised verdigris: its optical properties differ from those of the normal cupric acetate.

Aceto-arsenite of Copper. $C^2H^3O^2Cu.3AsO^2Cu$, or $C^4H^3O^3.CuO + 3(AsO^3.CuO)$.—*Schweinfurt green*, *Imperial green*, *Mitis green*, and when mixed with gypsum or heavy spar, *Neuwieder green*, *Mountain green*. Used as a pigment, and prepared on the large scale by mixing arsenious acid with cupric acetate and water. 5 parts of verdigris are made up to a thin paste, and added to a boiling solution of 4 parts or rather more of arsenious acid in 50 parts of water. The boiling must be well kept up, otherwise the precipitate assumes a yellow-green colour, from formation of arsenite of copper; in that case, acetic acid must be added, and the boiling continued a few minutes longer. The precipitate then becomes crystalline, and acquires the fine green colour peculiar to the aceto-arsenite. The salt is insoluble in water, and when boiled with water for a considerable time, becomes brownish and gives up acetic acid. Acids abstract the whole of the copper, and aqueous alkalis first separate blue cupric hydrate, which when boiled with the liquid, is converted into black cupric oxide, and afterwards into red cuprous oxide, an alkaline arsenate being formed at the same time.

ACETATES OF IRON.—*a. Ferrous Acetate.* When metallic iron or the protosulphide is dissolved in strong acetic acid, and the solution concentrated, small colourless silky needles are obtained, which dissolve easily in water, and rapidly absorb oxygen from the air.

β. *Ferric Acetate.*—Obtained by dissolving ferric hydrate in acetic acid, or by decomposing a solution of ferric sulphate with acetate of lead. It is uncrystallisable and very soluble in water, forming a red-brown solution; soluble also in alcohol. The aqueous solution, when kept in a state of ebullition for about 12 hours, undergoes a remarkable modification, acquiring a brick-red colour, and remaining clear when viewed by transmitted light, but appearing opaque and opalescent by reflected light. At the same time, it loses entirely the metallic taste of iron salts, and acquires that of vinegar; it forms a brown instead of a blue precipitate with ferrocyanide of potassium, and no longer exhibits the characteristic red colour with sulphocyanides. Traces of sulphuric or phosphoric acid, or of alkaline salts, precipitate the whole of the iron in the form of a red-brown precipitate, which, at ordinary temperatures, is perfectly insoluble in acids, even the most concentrated; hydrochloric and nitric acids throw down a red granular precipitate, which, when perfectly freed from the acid mother-liquor, dissolves easily and completely in water. (Péan de St. Gilles, Ann. Ch. Phys. [3] xlvi. 47.)

A mixture of the two acetates of iron, called *pyrolignite of iron* (*liqueur de ferraille, bouillon noir*), is prepared on the large scale by treating iron with wood-vinegar, in contact with the air. It is used as a mordant for black dyes; also for preserving wood.

Acetates of Lead.— The normal acetate $C^2H^3O^2Pb$, or $PbO.C^4H^3O^3$ (*Sugar of lead, saccharum Saturni, sel de Saturne, Bleizucker*) is prepared by dissolving oxide or carbonate of lead in acetic acid, wood-vinegar being used on the large scale, or by immersing plates of lead in vinegar in vessels exposed to the air. It crystallises in prisms containing $2C^2H^3O^2Pb + H^2O$, and belonging to the monoclinic system. Ordinary combination: $\infty P . 0P . \infty P \infty$, sometimes with the face $0P$ predominating, so as to give the crystals a tabular form. The length of the orthodiagonal is to that of the clino-diagonal, as 0·4197 to 1. Inclination of the axes = 70° 28′. Inclination of the faces: $\infty P : \infty P = 128°$; $\infty P : \infty P \infty = 116°$; $\infty P : 0P = 98° 30'$; $0P : \infty P \infty = 109° 32$. Cleavage parallel to $0P$ and $\infty P \infty$. The crystals are efflorescent, soluble in 0·59 parts of water at 15°·5 (60° F.), and in 8 parts of alcohol. The salt has a sweet, astringent taste, and is very poisonous. It melts at 75°·5; begins to give off water with a portion of its acid a little above 100°; and is completely dehydrated at 280°. Above that temperature it decomposes, giving off acetic acid, carbonic anhydride, and acetone, and leaving metallic lead very finely divided and highly combustible. The aqueous solution is partially decomposed by the carbonic acid of the air, carbonate of lead being precipitated, and a portion of acetic acid set free, which prevents further decomposition. The solution is not precipitated by ammonia in the cold, but yields crystals of oxide of lead when heated with a large excess of ammonia. Normal acetate of lead forms crystalline compounds with chloride of lead and with peroxide of lead.

(Berzelius, Ann. Chim. xciv. 292; Schindler, Brande's Archiv, xli. 129; Payen, Ann. Ch. Phys. [2] lxv. 238, and lxvi. 37; Wittstein, Buchner's Repert. lxxxiv. 170; Gm. viii. 310; Gerh. i. 736.)

Four *basic acetates* of lead have been described, viz.:

The sesquibasic acetate	.	$(C^2H^3O^2Pb)^4 . Pb^2O$	or $(C^4H^3O^3)^2 . (PbO)^3$.
The dibasic „	.	$(C^2H^3O^2Pb)^2 . Pb^2O$	or $C^4H^3O^3 . (PbO)^2$.
The tribasic „	.	$C^2H^3O^2Pb . Pb^2O$	or $C^4H^3O^3 . (PbO)^3$.
The sexbasic „	.	$(C^2H^3O^2Pb)^2 . (Pb^2O)^5$	or $C^4H^3O^3 . (PbO)^6$.

All of these however, except the tribasic salt, are of rather doubtful composition.

The *sesquibasic salt* is obtained by heating the normal salt till it melts, and subsequently solidifies in a white porous mass. By dissolving the residue in water and evaporating, the salt is then obtained in nacreous laminæ containing $2 [(C^2H^3O^2Pb)^4 . Pb^2O] + H^2O$. It is more soluble in water and alcohol than the normal acetate, and forms alkaline solutions. (Payen, Schindler.)

The *dibasic acetate* is deposited in the crystalline form when oxide of lead (massicot) is dissolved in the proper proportion in the normal acetate. The crystals contain 2 atoms water, half of which is given off at 70°, and the rest at 100°. (Schindler.)

The *tribasic acetate* is obtained in the crystalline form, when a solution of the normal salt saturated in the cold and mixed with $\frac{1}{5}$ of its volume of ammonia, is left to evaporate; also by digesting 7 parts of massicot in a solution of 6 parts of the crystallised normal acetate. It forms long silky needles, very soluble in water, but insoluble in alcohol. The aqueous solution becomes turbid on exposure to the air. According to Payen, the crystals contain $2(C^2H^3O^2Pb . Pb^2O) + H^2O$, but according to Berzelius, they are anhydrous.

The *sexbasic salt* is obtained by digesting the solution of either of the preceding salts with excess of oxide of lead. A crystalline precipitate is then formed, which dissolves sparingly in boiling water, and separates in silky needles containing $2[(C^2H^3O^2Pb)^2.(Pb^2O)^5] + 3H^2O$. (Berzelius.)

The liquid called *Goulard's lotion, lead-vinegar, acetum Saturni*, is a mixture of the aqueous solutions of these basic acetates of lead, chiefly the tribasic salt. It is prepared by digesting oxide of lead in acetic acid, or in a solution of the normal acetate. It is an alkaline liquid which is decomposed by the carbonic acid in the air. It precipitates a large number of vegetable substances, such as gum-resins, colouring matters, &c. and from its power of coagulating mucus, is much used as a lotion for wounds and sores.

Acetate of Lithium. $C^2H^3O^2Li + 2H^2O$.—Right rhomboïdal prisms, deliquescent in moist air, soluble in less than a third of their weight of water at 15°, and in 4·6 pts. of alcohol of sp. gr. 0·81 at 14°.

Acetate of Manganese.—Pale rose-coloured splinters or small prisms grouped together; soluble in 3 pts. of water.

Acetates of Mercury.—*Mercurous acetate*, $C^2H^3O^2,Hhg$, [$Hhg = Hg^2 = 200$], is obtained by precipitating mercurous nitrate with a soluble acetate. It forms anhydrous micaceous laminæ, sparingly soluble in water. Heat decomposes it into metallic mercury, carbonic anhydride, and acetic acid.

Mercuric Acetate, $C^2H^3O^2Hg$ [or $C^4H^3O^3.HgO$], is prepared by dissolving red oxide of mercury in warm acetic acid. It crystallises in brilliant micaceous laminæ, soluble in their own weight of water at 10°, and somewhat more soluble in boiling water. Alcohol and ether decompose it, separating mercuric oxide.

Acetate of Mercurammonium, $C^2H^3O^2.(NH^3Hg) + H^2O$, is obtained by agitating recently precipitated mercuric oxide with a solution of acetate of ammonium. It crystallises in rhomboïdal plates, very soluble in water, insoluble in alcohol. At 100° it gives off from 30 to 31 per cent. of its weight, and is converted into *acetate of tetramercurammonium*, $C^2H^3O^2(NHg^4)$.

Acetate of Nickel crystallises in apple-green prisms, slightly efflorescent, soluble in 6 pts. of cold water, insoluble in alcohol. The solution is decomposed by hydrosulphuric acid, which throws down sulphide of nickel.

Acetates of Potassium.—*Normal acetate.* $C^2H^3O^2K$ [or $C^4H^3O^3.KO$]. (*Terra foliata Tartari, Arcanum Tartari, Tartarus regeneratus, Blättererde, geblätterte Weinsteinerde*).

This salt exists in the juices of many plants. It is prepared by dissolving carbonate of potassium in acetic acid. When brown vinegar is used for the purpose, the carbonate of potassium should be added by small portions, so as to keep the solution constantly acid. The object of this precaution is to avoid the formation of coloured products by the contact of free alkali with the foreign matters in the vinegar. Pure acetate of potassium is a white salt, difficult to crystallise, very soluble in water and deliquescent, soluble also in alcohol, and precipitated by ether from the alcoholic solution. Carbonic acid gas, passed into a solution of the salt in absolute alcohol, throws down carbonate of potassium, and liberates acetate of ethyl. The salt melts below a red heat, forming a limpid oil, which solidifies in an extremely deliquescent mass on cooling. It requires a very high temperature to decompose it, and then gives off acetone, empyreumatic oil, and inflammable gases, and leaves a residue of carbonate of potassium mixed with charcoal. Heated with excess of hydrate of potassium, it yields carbonate of potassium and marsh gas:

$$C^2H^3O^2K + KHO = CH^4 + CO^3K^2.$$

Heated with arsenious anhydride, it yields cacodyl. (See Arsenides of Methyl.) Chlorine, passed into the aqueous solution of acetate of potassium, liberates carbonic anhydride, and forms a bleaching liquid, which however loses its decolorising power on exposure to the air. When an electric current is passed through a strong aqueous solution of acetate of potassium separated into two parts by a porous diaphragm, hydrogen alone is evolved at the negative pole; while, at the positive pole, there is evolved a gaseous mixture of methyl and carbonic anhydride, together with acetate of methyl and a small quantity of oxide of methyl. The principal decomposition is represented by the equation:

$$C^2H^4O^2 = CH^3 + CO^2 + H,$$

the acetate and oxide of methyl being secondary products. (Kolbe, Ann. Ch. Pharm. lxix. 257.)

Acid Acetate or *Diacetate of Potassium*, $C^2H^3O^2K.C^2H^4O^2$, [or $C^4H^3O^3.HO + C^4H^3O^3.KO$.]

When the normal acetate is evaporated with an excess of strong acetic acid, this acid salt is deposited in needles or laminæ, or by slow evaporation in long flattened prisms, apparently belonging to the rhombic system. It is very deliquescent, melts at 148°, and decomposes at 200°, giving off crystallisable acetic acid. On this property is founded an easy method of obtaining the crystallisable acid.

Diacetate of potassium is formed when the normal acetate is distilled with butyric or valerianic acid; but neither of these acids decomposes the salt thus produced. Hence, when butyric or valerianic acid is mixed with acetic acid, a separation more or less complete may be effected by half neutralising the liquid with potash, and distilling. If the acetic acid is in excess, diacetate of potassium alone remains behind, the whole of the valerianic or butyric acid passing over, together with the remainder of the acetic acid. If, on the contrary, the other acid is in excess, it passes over, unmixed with acetic acid, and the residue consists of diacetate of potassium mixed with butyrate or valerate. By repeating the process a certain number of times, either on the acid distillate or on the acid separated from the residue by distillation with sulphuric acid, complete separation may be effected. (Liebig, Ann. Ch. Pharm. lxxi. 355.)

Anhydrous Diacetate of Potassium, $2C^2H^3O^2K.C^4H^6O^3$ [$=KO.\ 2C^4H^3O^3$] is produced by dissolving melted acetate of potassium in acetic anhydride at the boiling heat, or by the action of potassium on acetic anhydride. Forms colourless needles very soluble in water, less deliquescent than normal acetate of potassium. It is decomposed by heat, giving off acetic anhydride. (Gerhardt, Ann. Ch. Phys. [3] xxxvii. 317.)

ACETATE OF SILVER, $C^2H^3O^2Ag$.—Obtained by precipitating nitrate of silver with acetate of sodium. Crystallises from boiling water in thin, flexible laminæ; soluble in 100 pts. of cold water.

ACETATE OF SODIUM, $C^2H^3O^2Na$ [or $C^4H^3O^3.NaO$.] *Terra foliata tartari crystallisabilis, Terre foliée minérale.*—Prepared either by dissolving carbonate of sodium in acetic acid, or by decomposing acetate of calcium with sulphate of sodium. Forms large transparent prisms belonging to the monoclinic system. Ordinary combination: $\infty P . [\infty P \infty] . 0P . -P$; more rarely with $\infty P \infty$, $+P$, $+2P\infty$. Ratio of the axes: $a : b : c = 0{\cdot}8348 : 1 : 0{\cdot}8407$. Angle of the axes $= 68° 16'$. Inclination of the faces: $\infty P : \infty P$ in the plane of the orthodiagonal and principal axis $= 95°{\cdot}30$; $-P : +P$, forming the obtuse edges of the pyramid $+P$ in the plane of the oblique diagonal and principal axis $= 117°{\cdot}32$; $\infty P : 0P = 75°{\cdot}35$. Cleavage parallel to $0P$ and ∞P. (Gerhardt, Traité i. 725.) The crystals contain 3 at. water. They effloresce slightly in dry air, completely at a moderate heat, and melt below 100°. They dissolve in 3·9 pts. of water at 6°, in 2·4 pts. at 37°, and in 1·7 pts. at 48° (Osann). According to Berzelius, a solution saturated at the boiling heat, contains 0·48 pts. water to 1 pt. of salt, and boils at 124°·4. The salt is less soluble in alcohol. It has a bitter, pungent, but not disagreeable taste.

ACETATE OF STRONTIUM crystallises like the barium-salt in two different forms, containing different quantities of water. The salt deposited at 15°, contains 4·23 p. c. water (? $4C^2H^3O^2Sr + H^2O$), and that which is deposited at low temperatures contains $C^2H^3O^2Sr + H^2O$. The latter forms prisms belonging to the monoclinic system, $\infty P : \infty P = 124° 54'$; $\infty P . \infty P\infty = 107° 33'$; $0P : P\infty = 153°{\cdot}12$. Cleavage indistinct, parallel to $\infty P\infty$.

ACETATE OF TIN.—Boiling acetic acid dissolves tin slowly, with evolution of hydrogen; the hydrated protoxide dissolves easily in the boiling acid, and the solution evaporated to a syrup and covered with alcohol yields small colourless crystals. Hydrated dioxide of tin also dissolves in acetic acid, and the solution yields a gummy mass when evaporated. Dichloride of tin forms a crystalline compound with glacial acetic acid.

ACETATE OF URANIUM.—*Uranous Acetate*, obtained by evaporating a solution of oxide in acetic acid, crystallises in green needles grouped in warty masses.

Uranic Acetate, or *Acetate of Uranyl*, $C^2H^3O^2(U^2O)$* [$= C^4H^3O^3.U^2O^3$], is obtained by heating uranic nitrate till it begins to evolve oxygen, dissolving the yellowish red mass, which still contains nitric acid, in warm concentrated acetic acid, and evaporating to the crystallising point; all the nitric acid then remains in the mother liquid. From a very concentrated, or from an acid solution slightly cooled, the salt separates in beautiful rhomboïdal prisms, $C^2H^3O^2(U^2O) + H^2O$, belonging to the monoclinic system; boiling water decomposes them with separation of uranic hydrate, but the solution yields the same crystals by evaporation. A more dilute solution cooled below 10° deposits square-based octahedrons containing $C^2H^3O^2(U^2O) + \frac{3}{2} H^2O$, or

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* Uranyl, U^2O, is a monatomic radicle, supposed to exist in the uranic compounds. (See URANIUM.)

$2C^2H^3O^2(U^2O) + 3H^2O$. They give off $\frac{1}{3}$ of their water at 200°, and the rest at 275°, leaving the yellowish red anhydrous salt.

Uranic acetate combines with the acetates of the more basic metals, forming double acetates. The *ammonium*, *potassium*, and *sodium* salts are obtained by adding the solutions of the carbonates to a solution of uranic acetate, till a precipitate is formed consisting of a uranate of the alkali-metal, redissolving this precipitate in a slight excess of acetic acid, and cooling the solution till it crystallises. The other double salts of this group are obtained by boiling the carbonates with uranic acetate, till the whole of the uranic oxide is precipitated, redissolving the precipitate in acetic acid, and evaporating. The *lead* and *cadmium* salts consist of 1 at. of uranic acetate combined with 1 at. of the monobasic acetate, their formula being $C^2H^3PbO^2 . C^2H^3(U^2O)O^2 + 3H^2O$ and $C^2H^3CdO^2.C^2H^3(U^2O)O^2 + \frac{5}{2} H^2O$. All the rest contain 2 at. uranic acetate with 1 at. of the monobasic metal, their general formula being $C^2H^3MO^2. 2C^2H^3(U^2O)O^2 + nH^2O$. Most of these salts crystallise with facility, the potassium and silver salts in the quadratic system; the sodium salt forms regular tetrahedrons. The strontium and calcium salts are very soluble in water, and difficult to crystallise. The sodium salt is anhydrous; the rest contain water of crystallisation. (Wertheim, J. pr. Chem. xxix. 209; Weselsky, Chem. Gaz. 1858, 390.)

ACETATE OF YTTRIUM, $C^2H^3O^2Y + H^2O$.—Rhomboïdal prisms with trihedral summits. They are permanent in the air at ordinary temperatures; give off their water, and become opaque at 100°; dissolve in 9 pts. of cold water, and in a smaller quantity of boiling water; also in alcohol. (Berlin.)

ACETATE OF ZINC, $C^2H^3O^2Zn + \frac{3}{2}H^2O$, or $2C^2H^3O^2 Zn + 3H^2O$ [$= C^4H^3ZnO^4 + 3HO$].—Obtained by dissolving either the metal, the oxide, or the carbonate in acetic acid. Crystallises in nacreous efflorescent laminæ belonging to the monoclinic system (Kopp's Krystallographie, p. 310). Ordinary combination: $0P . \infty P . \infty P\infty . +P . +2P\infty$, the face $0P$ predominating. $a : b : c = 0{\cdot}4838 : 1 : 0{\cdot}87$. Inclination of axes = 46°30′. Inclination of faces, $\infty P : \infty P$ in the plane of orthodiagonal and principal axis = 112° 36′; $\infty P . 0P = 112° 28′$; $0P : \infty P\infty = 113° 30′$; $0P : P\infty = 80°$; $0P : +P = 75° 30′$. Cleavage parallel to $0P$. The salt dissolves very readily in water. At 100° it melts, gives off its water with a little acetic acid, then solidifies, and does not liquefy again till heated to 190° or 195°, at which temperature anhydrous acetate of zinc sublimes in nacreous scales. At higher temperatures, complete decomposition ensues. (Larocque, Recueil des Trav. de la Soc. Pharm. 1847–54.)

ACETIC ACID, SUBSTITUTION PRODUCTS OF.—The following acids (which will be more fully described hereafter), are derived from acetic acid by substitution:

Bromacetic acid	$\left.\begin{matrix}C^2H^2BrO\\H\end{matrix}\right\}O$
Dibromacetic acid	$\left.\begin{matrix}C^2HBr^2O\\H\end{matrix}\right\}O$
Chloracetic acid	$\left.\begin{matrix}C^2H^2ClO\\H\end{matrix}\right\}O$
Trichloracetic acid	$\left.\begin{matrix}C^2Cl^3O\\H\end{matrix}\right\}O$
Iodacetic acid	$\left.\begin{matrix}C^2H^2IO\\H\end{matrix}\right\}O$
Diniod-acetic acid	$\left.\begin{matrix}C^2HI^2O\\H\end{matrix}\right\}O$
Thiacetic acid	$\left.\begin{matrix}C^2H^3O\\H\end{matrix}\right\}S$

The brominated and chlorinated acids are produced by the direct action of bromine and chlorine on acetic acid; the iodated acids by the action of iodide of potassium on bromacetate and dibromacetate of ethyl; and thiacetic acid by treating glacial acetic acid with pentasulphide of phosphorus (p. 11). All these acids are monatomic, like acetic acid itself, correspond to it in nearly all their reactions, and are formed upon the same type.

ACETIC ANHYDRIDE. $C^4H^6O^3 = (C^2H^3O)^2O$. *Anhydrous Acetic acid; Oxide of Acetyl; Acetate of Acetyl.*—(Gerhardt, Traité, i. 711.)

This compound is obtained: 1. By the action of oxychloride of phosphorus, $POCl^3$, on acetate of potassium. The acetate deprived of water by fusion, is introduced into a tubulated retort, and the oxychloride of phosphorus admitted through the tubulus, drop by drop. A violent action takes place, the mixture becoming very hot without the application of external heat, and a liquid distils over, which is the chloride of acetyl, while tribasic phosphate of potassium remains in the retort:

$$3C^2H^3KO^2 + POCl^3 = PO^4K^3 + 3(C^2H^3O.Cl).$$

If now this liquid be poured back again three or four times into the retort, so that it may remain for some time in contact with the acetate of potassium, that salt being also in excess and pretty strongly heated, a further action takes place between the acetate of potassium and the compound $C^2H^3O.Cl$, the result of which is the formation of acetic anhydride: thus,

$$C^2H^3KO^2 + C^2H^3O.Cl = KCl + C^4H^6O^3.$$

The acetic anhydride enters into combination with the acetate of potassium, and a considerable degree of heat is required to destroy this compound and cause the anhydride to distil over. The distillate is more or less contaminated with acetic acid and chloride of acetyl; but on redistilling the crude product, these impurities pass over at the commencement, before the temperature rises to 137°·5, after which the pure anhydride distils over.—2. By the action of terchloride of phosphorus on acetate of potassium. When the liquid chloride is added drop by drop to the acetate of potassium (about 1 pt. PCl^3 to more than 2 pts. of the acetate), the action begins without application of heat, and chloride of acetyl, amounting in quantity to about half the chloride of phosphorus used, distils over mixed with a small quantity of chloride of phosphorus. On heating the residue after this action has ceased, acetic anhydride distils over free from chloride, and in quantity equal to about a third of the chloride of phosphorus used. The product contains a small quantity of a phosphorus-compound, which causes it to impart a brownish colour to nitrate of silver; but it may be freed from this impurity by a second distillation with acetate of potassium. — 3. By the action of chloride of benzoyl, $C^7H^5O.Cl$, on fused acetate of potassium. The first products of the action are chloride of potassium and acetate of benzoyl, $C^9H^8O^3$:

$$C^7H^5O.\,Cl + C^2H^3KO^2 = KCl + \left.\begin{matrix}C^7H^5O\\C^2H^3O\end{matrix}\right\}O.$$

But if the acetate of potassium is in excess, and the mixture is heated somewhat above the temperature at which the original substances act upon each other, a further action takes place, and a colourless liquid distils over, which is acetic anhydride, while benzoic anhydride remains in the retort in combination with benzoate of potassium. These new products are formed by double decomposition between 2 atoms of the benzoic acetate:

$$2\left\{\begin{matrix}C^7H^5O\\C^2H^3O\end{matrix}\right\}O = \left.\begin{matrix}C^7H^5O\\C^7H^5O\end{matrix}\right\}O + \left.\begin{matrix}C^2H^3O\\C^2H^3O\end{matrix}\right\}O$$

4. By the action of chloride of acetyl, C^2H^3OCl, on dry benzoate of sodium. The reaction, which takes place without the aid of heat, is precisely similar to the preceding.

Acetic anhydride is a colourless, very mobile, strongly refracting liquid, having a powerful odour, similar to that of the hydrated acid, but stronger, and recalling at the same time that of the flowers of the white-thorn. Sp. gr. 1·073 at 20°·5, which is nearly that of the hydrated acid, $C^2H^4O^2 + H^2O$, at its greatest density. Boiling point 137°·5 under a pressure of 750 mm. Vapour density = 3·47 (by calculation 3·531 for a condensation to 2 volumes).

Fuming sulphuric acid becomes heated by contact with acetic anhydride, carbonic anhydride being given off and a conjugated acid produced, which forms a gummy salt with lead. *Potassium* acts violently on acetic anhydride, evolving a gas which does not take fire if the potassium be introduced by small portions at a time. The liquid, after a while, solidifies into a mass of needles, consisting of a compound of acetic anhydride with acetate of potassium (p. 33). An oily substance is also produced, having a very pleasant ethereal odour. Finely divided *zinc* acts upon acetic anhydride in a similar manner, but less energetically, and only when heated in the water bath; hydrogen gas is then given off, and a soluble salt formed, which is deposited in microscopic crystals on the surface of the metal, and greatly retards the action. On saturating the excess of acetic acid in the residue with carbonate of sodium, the ethereal odour above mentioned is perceived. The hydrogen evolved, if collected immediately, has the same odour, burns with a bluish flame, and the product of the combustion renders lime-water turbid; but after passing through potassium, it is inodorous, and when burnt yields nothing but pure vapour of water.

Acetic anhydride does not combine immediately with *water*, but when poured into that liquid, falls to the bottom in oily drops which dissolve after a while, if the liquid is heated or agitated. It absorbs water from the air, and must therefore be kept in well closed vessels.

Acetic anhydride combines with *aldehydes.* With ordinary aldehyde, it forms a liquid compound, $C^4H^6O^3.\ C^2H^4O$ (Geuther), and a similar compound with valeral. $C^4H^6O^3.\ C^5H^{10}O$ (Guthrie and Kolbe); also with bitter almond oil (Geuther).

ACETOBENZOIC, OR BENZOACETIC ANHYDRIDE, $C^9H^8O^3 = \left.\begin{matrix}C^2H^3O\\C^7H^5O\end{matrix}\right\}O$. *Acetate of Benzoyl, Benzoate of Acetyl.*—Obtained by the action of chloride of acetyl on benzoate of sodium. Heavy oil smelling like Spanish wine. Neutral to litmus. Boils at 120° C. and is resolved into acetic and benzoic anhydrides (p. 35). Resolved into acetic and benzoic acids by boiling with water, and more quickly with alkalis.

ACETO-CINNAMIC ANHYDRIDE, $C^2H^3O.C^9H^7O.O$. *Acetate of Cinnamyl, &c.*—A very instable product obtained by the action of chloride of acetyl on cinnamate of sodium. Oil heavier than water, something like the preceding compound.

ACETO-CUMINIC ANHYDRIDE, $C^2H^3O\ .\ C^{10}H^{11}O\ .\ O$. *Acetate of Cumyl.*—Resembles the preceding compounds. In the moist state it quickly turns acid, and yields beautiful laminæ of cuminic acid, the odour of acetic acid becoming perceptible at the same time.

ACETO-SALICYLIC ANHYDRIDE, $C^2H^3O\ .\ C^7H^5O^2.O$. *Acetate of Salicyl, &c.*—Salicylate of sodium is strongly attacked by chloride of acetyl, even at ordinary temperatures, the mixture liquefying at first, but becoming perfectly hard in a few seconds. The product dissolves with effervescence in carbonate of sodium, the anhydride being converted into acetate and salicylate of sodium. (Gerhardt, Traité, iii. 319.)

ACETIC ETHERS. These compounds are the acetates of the alcohol-radicles, and may be divided into the following groups:

1. Monatomic Acetic Ethers.

ACETATE OF ALLYL, $C^2H^3O.C^3H^5$.—Prepared by treating acetate of silver with iodide of allyl, and rectifying once or twice over acetate of silver. It is a colourless liquid, lighter than water, having a pungent, aromatic odour, and boiling between 98° and 100°. Boiling potash decomposes it into acetate of potassium and allyl-alcohol. (Cahours and Hofmann, Chem. Soc. Qu. J. x. 322.)

ACETATE OF AMYL, OR ACETATE OF PENTYL, $C^2H^3O^2.C^5H^{11}$.—This compound is slowly produced when amylic alcohol is left in contact with acetic acid, and may be conveniently prepared by distilling 2 pts. of acetate of potassium, or 3 pts. of dehydrated acetate of lead, with 1 pt. of strong sulphuric acid, and 1 pt. of amylic alcohol, agitating the distillate with milk of lime, then dehydrating over chloride of calcium, and rectifying. It is a transparent, colourless liquid, of sp. gr. 0·8572 at 21°, and boiling at 133·3°, under a pressure of 27″ 8‴, with a platinum wire immersed in it. Vapour-density 4·458. Odour ethereal and aromatic, like that of acetate of ethyl. It is insoluble in water, but dissolves in *alcohol*, *ether*, and *fusel oil*. It is decomposed very slowly by aqueous potash, but quickly by alcoholic potash, yielding amylic alcohol and acetate of potassium. Chlorine passed through it at 100°, converts it into *di-chlorinated acetate of amyl*, $C^7H^{12}Cl^2O^2$, and this, by the action of chlorine in sunshine, is converted into a higher chlorine-compound.

ACETATE OF BENZYL, $C^2H^3O^2.C^7H^7$.—Produced by treating 2 vol. benzyl-alcohol with a mixture of 1 vol. sulphuric acid and 4 or 5 vol. acetic acid, or by boiling chloride of benzyl with alcoholic acetate of potassium. Colourless oil, heavier than water, and having a very agreeable odour, like that of pears. Boils at 210° C. Boiled with potash-ley, it yields acetate of potassium and benzylic alcohol. (Cannizzaro, Ann. Ch. Pharm. lxxxviii. 130.)

ACETATE OF ETHYL. *Acetic ether, Ethylic Acetate, Essigäther, Essignaphtha, Essigsaures Æthyloxyd, Ether acétique.* $C^4H^8O^2 = C^2H^3O^2.C^2H^5$. or $C^4H^3O^3.C^4H^5O$. (Lauragais, Journ. d. Sçavans, 1759, 324; Thénard, Mém. d'Arcueil, i. 153; Dumas and Boullay, J. Pharm. xiv. 113; Liebig, Ann. Ch. Pharm. v. 34; xxx. 144; Gm. viii. 493; Gerh. i. 743).—Discovered by Lauragais in 1759. It is formed by heating alcohol with acetic acid, or with an acetate and strong sulphuric acid, or by distilling ethyl-sulphate of calcium or potassium with glacial acetic acid. The best mode of preparing it is to distil a mixture of 3 pts. of acetate of potassium, 3 pts. of absolute alcohol, and 2 pts. of sulphuric acid; or 10 pts. of acetate of sodium, 6 pts. of alcohol, and 15 pts. of sulphuric acid; or 16 pts. of dry acetate of lead, 4½ pts. of alcohol, and 6 pts. of sulphuric acid. The acid is first mixed with the alcohol, and the liquid poured upon the salt reduced to fine powder. The mixture is then distilled to dryness, the heat being moderate at first, but increased towards the end of the process. The product is purified by digesting it with chloride of calcium and rectifying the decanted liquid.

Acetate of ethyl is a colourless liquid, having a pleasant ethereal odour. Sp. gr. 0·91046 at 0° (Kopp); 0·932 at 20° (Gössmann). Boils at 74°·3, when the barometer stands at 760 mm. (Kopp). Vapour-density 3·06 (Boullay and Dumas). It dissolves in 11 or 12 pts. of water, at ordinary temperatures (Mohr, Arch. Pharm. [2] lxv. 1), in all proportions of alcohol and ether. It burns with a yellowish flame, giving off the odour of acetic acid, and leaving that acid in the liquid state. It is permanent when dry, but in the moist state gradually decomposes into alcohol and acetic acid. The same decomposition takes place more quickly under the influence of alkalis. Heated with strong sulphuric acid, it is resolved into oxide of ethyl and acetic acid. Hydrochloric acid converts it into acetic acid and chloride of ethyl.

Action of Chlorine on *Acetate of Ethyl.* (Malaguti, Ann. Ch. Phys. [2] xx. 367; ibid. [3] xvi. 2, 58; Leblanc, ibid. [3] 197; Cloez, ibid. [3] xvii. 304.,—When acetate of ethyl is introduced into a bottle filled with dry chlorine gas, in the proportion of 1 atom acetate of ethyl to 8 atoms chlorine, and the action allowed to go on, first in the shade and afterwards with continually greater exposure to sunshine, a number of chlorinated compounds are formed in which 2, 3, 4, 5, 6, 7, and 8 atoms of hydrogen in the acetate of ethyl are successively replaced by an equal number of chlorine-atoms. It is however not always possible to obtain the particular compound required, the compounds $C^4H^6Cl^2O^2$, $C^4HCl^7O^2$, and $C^4Cl^8O^2$, being the only ones that can be produced with certainty. Other products are also formed, among which are acetic acid, trichloracetic acid, and sesquichloride of carbon. If the acetate of ethyl is at once exposed to sunshine in contact with chlorine, an explosion takes place, attended with deposition of charcoal.

Dichlorinated Acetate of Ethyl, $C^4H^6Cl^2O^2$, is the product obtained when the acetate of ethyl is kept cool and in the shade during the action of the chlorine. On distilling the product to separate the more volatile portions, till the boiling point rises to 110°, washing the brownish residue with water, and drying it over lime and sulphuric acid, the compound is obtained as a transparent colourless oil, of sp. gr. 1·301 at 12°. It smells somewhat like acetic acid, has a peppery taste, and produces irritation in the throat. It is slowly decomposed by water, yielding hydrochloric and acetic acids. $C^4H^6Cl^2O^2 + 2H^2O = 2C^2H^4O^2 + 2HCl$; slowly also by aqueous potash, but quickly by alcoholic potash, yielding acetate and chloride of potassium. (Malaguti.)

Trichlorinated Acetate of Ethyl, $C^4H^5Cl^3O^2$, was obtained by exposing the dichlorinated compound for some time to the action of chlorine in a bottle, covered at the upper part with black paper, so that the light fell only on the lower part of the liquid. It resembles the preceding compound, but cannot be distilled without alteration. It is isomeric with trichloracetate of ethyl, $C^2Cl^3O^2.C^2H^5$. See TRICHLORACETIC ACID. (Leblanc.)

Tetrachlorinated Acetate of Ethyl, $C^4H^4Cl^4O^2$, was obtained by exposing the dichlorinated compound to the sun in autumn, in bottles filled with dry chlorine. After rectification, washing, and drying, it forms an oil of sp. gr. 1·485 at 25°. It is decomposed by potash, yielding chloride, acetate, and trichloracetate of potassium (Leblanc). The *five-chlorine compound,* $C^4H^3Cl^5O^2$, was obtained in the same manner as the preceding, excepting that the gas above the liquid was protected from the action of the solar rays; the *six-chlorine compound* $C^4H^2Cl^6C^2$, by exposing the last compound to the sun for two days, in a bottle filled with dry chlorine. Sp. gr. 1·698 at 23·5. The *seven-chlorine compound,* $C^4HCl^7C^2$, was produced by exposing the dichlorinated compound in bottles filled with dry chlorine, to the sun for some months in winter. It forms rather soft crystals, insoluble in water, sparingly soluble in cold alcohol of ordinary strength, very soluble in ether. They melt below 100°, but do not appear to be volatile without decomposition. An oily liquid isomeric with this compound, and having a sp. gr. of 1·692 at 24·5°, is obtained by exposing trichloracetate of ethyl to chlorine in the shade, as long as any action goes on. (Leblanc.)

Perchlorinated Acetate of Ethyl, $C^4Cl^8O^2$, is prepared by exposing di- or tri-chlorinated acetate of ethyl to the brightest summer sunshine, and at the same time heating it to 110°; even then the substitution takes place very slowly (Leblanc). The product is distilled in an atmosphere of carbonic acid, to remove free chlorine. It is a colourless oil, which remains liquid at a few degrees below 0°, and has a strong pungent odour like that of chloral. Sp. gr. 1·79 at 25°. Boils, with partial decomposition, at 245° (Leblanc). When its vapour is passed through a tube filled with fragments of glass, and heated to 400°, it is partly converted into the isomeric compound chloraldehyde, C^2Cl^4O (Malaguti). In contact with water or moist air, it is gradually decomposed, yielding trichloracetic and hydrochloric acids. A similar decomposition is instantly produced by strong aqueous potash (Leblanc):

$$C^4Cl^8O^2 + 2H^2O = 2C^2HCl^3O^2 + 2HCl.$$

Ammonia, either gaseous or dissolved in water, acts strongly on the compound, producing sal-ammoniac and trichloracetamide (Malaguti):

$$C^4Cl^8O^2 + 2NH^3 = 2HCl + 2C^2H^2Cl^3NO$$

With absolute alcohol, the compound becomes strongly heated, and is completely converted into hydrochloric acid and trichloracetate of ethyl (Malaguti):

$$C^4Cl^8O^2 + 2C^2H^6O = 2HCl + 2C^4H^5Cl^3O^2.$$

When exposed for a long time to the action of chlorine, it yields crystals of sesquichloride of carbon. (Leblanc.)

Perchloracetic ether may be regarded as a *trichloracetate of pentachlorethyl*, $C^2Cl^3O^2.C^2Cl^5$; and in like manner, all the preceding compounds which contain more than 3 atoms of chlorine, may be viewed as trichloracetates of ethyl-radicles, in which the H is more or less replaced by Cl: *e.g.* pentachloracetic ether, $C^4H^3Cl^5O^2 = C^2Cl^3O^2.C^2H^3Cl^2$. Some of them appear however to be susceptible of isomeric modifications.

ACETATE OF METHYL, $C^3H^6O^2 = C^2H^3O . CH^3$. *Methylic Acetate, Essigsaurer Holzäther.* (Dumas and Péligot (1835), Ann. Ch. Phys. lviii. 46.—Weidmann and Schweizer, Pogg. xliii. 593.—H. Kopp, Ann. Ch. Pharm. lv. 181.—Gm. viii. 484; Gerh. i. 741.)—This compound occurs in crude wood-vinegar (Weidmann and Schweizer). The liquid called *Æther lignosus* or *Spiritus pyroaceticus* appears to be impure acetate of methyl.

Preparation.—1. Two pts. of wood-spirit are distilled with 1 pt. of glacial acetic acid and 1 pt. sulphuric acid; the distillate is shaken up with chloride of calcium, the acetate of methyl then rising to the top; and this product is freed from sulphurous acid by agitation with quicklime, and from wood-spirit by 24 hours' contact with chloride of calcium, which takes up the latter substance (Dumas and Peligot). —2. When 1 part of wood-spirit is distilled with 1 pt. acetate of potassium and 2 pts. of sulphuric acid, acetate of methyl passes over first, then sulphurous acid, acetic acid, methylic oxide, and a small quantity of methylic sulphate. The first receiver must therefore be removed as soon as sulphurous acid begins to escape; its contents shaken up with water; and the separated ether rectified over chloride of calcium and quicklime (Weidmann and Schweizer).—3. A mixture of 3 pts. wood-spirit, 14½ pts. dehydrated acetate of lead, and 5 pts. sulphuric acid is distilled; the distillate is shaken up with milk of lime; and the stratum of methylic acetate which rises to the surface is dehydrated by repeated treatment with chloride of calcium, then decanted from the lower liquid, and rectified. (H. Kopp.)

Acetate of methyl is a colourless liquid, having a very agreeable odour, like that of acetate of ethyl, sp. gr. 9·0085 at 21°; 0·9562 at 0° (Kopp). Boiling point, 56·3° under a pressure of 760 mm. (Kopp, Pogg. Ann. lxii. 1); 55° under a pressure of 762 mm. (Andrews, Chem. Soc. Qu. J. i. 27). Vapour-density 2·563 (Dumas and Péligot), by calculation 2·564. Index of refraction 1·3576. (Delffs, Pogg. Ann. lxxxi. 470.)

Acetate of methyl dissolves in water, and mixes in all proportions with alcohol and ether. The aqueous solution suffers but little decomposition by boiling. Solutions of caustic alkalis convert the compound into wood-spirit and an alkaline acetate. When poured on pulverised soda-lime, it is decomposed with violence, yielding a mixture of acetate and formate of sodium, and giving off hydrogen. In contact with strong sulphuric acid, it becomes heated, gives off acetic acid, and forms methylsulphuric acid. With chlorine it forms a number of substitution-products.

Dichlorinated Acetate of Methyl, $C^3H^4Cl^2O^2$, is formed by passing dry chlorine gas through acetate of methyl, assisting the action by a gentle heat towards the end. It is purified like the corresponding ethyl-compound. It is a colourless neutral liquid, having a pungent odour; its taste is sweet at first, but afterwards alliaceous and burning. Sp. gr. 1·25. Boils between 145° and 148°, but begins to decompose and give off fumes at 138°. It burns with a yellow flame, edged with green at the bottom. It is decomposed slowly by water, quickly by aqueous potash, and violently by alcoholic potash, yielding formic, acetic, and hydrochloric acids:

$$C^3H^4Cl^2O^2 + 2H^2O = CH^2O^2 + C^2H^4O^2 + 2HCl.$$

This compound is isomeric if not identical with dichlorinated formate of ethyl. (Malaguti, Ann. Ch. Phys. [2] lxx. 379.)

Trichlorinated Acetate of Methyl, $C^3H^3Cl^3O^2$, is obtained by passing chlorine very slowly into acetate of methyl, as long as any decomposition takes place, and purifying the product by repeated fractional distillation. It is a colourless oily liquid, heavier than water, boiling at 145°, and distilling without decomposition. It is decomposed by caustic potash, yielding chloride and formate of potassium, and *chloromethylase*, CHCl:

$$C^3H^3Cl^3O^2 + 2K^2O = 2KCl + 2CHKO^2 + CHCl.$$

It is isomeric but not identical with trichloracetate of methyl, $C\,Cl^3O^2.\,CH^3$, produced by distilling wood-spirit with trichloracetic acid and a small quantity of sulphuric acid. (Laurent, Ann. Ch. Phys. [2] lxxiii. 25.)

Perchlorinated Acetate of Methyl, $C^3Cl^6O^2$. (Cloez, Ann. Ch. Phys. [3] xvii. 297, 311.)—This compound, which appears to be identical with perchlorinated formate of ethyl, is produced by exposing acetate of methyl to the action of chlorine in sunshine, as long as the gas continues to be absorbed. It is a colourless liquid, having a suffocating odour and a disagreeable taste, which soon becomes intolerably acid, from decomposition. Sp. gr. 1·705 at 18°. Boils at about 200°, with partial decomposition. It is quickly decomposed by water and by moist air, yielding hydrochloric, carbonic, and terchloracetic acids:

$$C^3Cl^6O^2 + 2H^2O = 3HCl + CO^2 + C^2HCl^3O^2.$$

Similarly by the fixed alkalis in solution. With aqueous ammonia, it forms trichloracetamide, together with chloride and carbonate of ammonium:

$$C^3Cl^6O^2 + 6NH^3 + 2H^2O = N.H^2.C^2Cl^3O + 3NH^4Cl + CO^3\,(NH^4)^2$$

With alcohol it forms hydrochloric acid, trichloracetate of ethyl, and monochlorinated formiate of methyl:

$$C^2Cl^6O^2 + 2C^2H^6O = 2HCl + C^2Cl^3O^2.C^2H^5 + C^2H^3ClO^2.$$

Similarly with wood-spirit it yields trichloracetate of methyl, and monochlorinated formate of methyl.

The vapour passed through a red-hot porcelain tube is decomposed into chloraldehyde and chloro-carbonic oxide (phosgene) gas:

$$C^3Cl^6O^2 = C^2Cl^4O + COCl^2.$$

Acetate of Octyl, $C^2H^3O^2.\,C^8H^{17}$.—Prepared by passing hydrochloric acid gas through a mixture of acetic acid and octylic (caprylic) alcohol; or, better by distilling a mixture of octylic alcohol, acetate of sodium, and sulphuric acid. It is a liquid of very agreeable odour, insoluble in water, boiling at 190°. (Bouis, Compt. rend. xxxviii. 937.)

Acetate of Phenyl, $C^2H^3O.C^6H^5$.—Produced by the action of chloride of acetyl on acetate of phenyl: also by boiling an alcoholic solution of phosphate of phenyl with acetate of potassium. After all the alcohol has evaporated, the temperature of the mixture rises rapidly, and acetate of phenyl distils over in the form of an oily liquid. It is heavier than water, and slightly soluble in that liquid. Boils at 190°. Boiling potash decomposes it, yielding acetate of potassium and hydrate of phenyl. (Scrugham, Chem. Soc. Qu. J. vii. 241.)

Acetate of Tetryl, or Acetate of Butyl, $C^2H^3O^2.\,C^4H^9$.—Obtained by heating iodide of tetryl with a slight excess of very dry acetate of silver in a sealed flask at 100°:—also by distilling in an oil-bath equivalent quantities of acetate of potassium (recently fused) and tetryl-sulphate of potassium:

$$C^2H^3O^2.K + SO^4.K.C^4H^9 = C^2H^3O^2.C^4H^9 + SO^4.K^2$$

Acetate of Trityl, or Acetate of Propyl, $C^2H^3O^2.C^3H^7$.—Obtained by distilling propylic alcohol with a mixture of acetic and sulphuric acid. Resembles acetate of ethyl. Boils at 90°. (Berthelot.)

It is a colourless liquid of agreeable odour. Sp. gr. 0·8845 at 16° C. Boils at 114°. Vapour-density 4·073 (calculation, 4·017). Boiling potash converts it into acetate of potassium and tetrylic alcohol.

2. Diatomic Acetic Ethers. (*Glycolic Ethers.*)—These compounds are derived from the diatomic alcohols or glycols by the substitution of 1 or 2 at. acetyl ($C^2H^3O = Ac$), for 1 or 2 at hydrogen. They are related to the glycols in the same manner as the monatomic acetic ethers just described are related to the monatomic alcohols. The following have been obtained:—

Monoacetate of Ethylene	$\left.\begin{matrix}(C^2H^4)''\\ Ac.H\end{matrix}\right\}O^2$	Diacetate of Butylene	$\left.\begin{matrix}(C^4H^8)''\\ Ac^2\end{matrix}\right\}O^2$
Diacetate of Ethylene	$\left.\begin{matrix}(C^2H^4)''\\ Ac^2\end{matrix}\right\}O^2$	Diacetate of Amylene	$\left.\begin{matrix}(C^5H^{10})''\\ Ac^2\end{matrix}\right\}O^2$
Diacetate of Propylene	$\left.\begin{matrix}(C^3H^6)''\\ Ac^2\end{matrix}\right\}O^2$	Diacetate of Benzylene	$\left.\begin{matrix}(C^7H^6)''\\ Ac^2\end{matrix}\right\}O^2$

The diacetates are produced by the action of acetate of silver on the chlorides, bromides, or iodides of the several diatomic alcohol-radicles: *e.g.*

$$\underbrace{C^2H^4Br^2}_{\text{Bromide of ethylene.}} + \underbrace{\left.\begin{matrix}(C^2H^3O)^2\\ Ag^2\end{matrix}\right\}O^2}_{\text{2 at. acetate of silver.}} = 2AgBr + \underbrace{\left.\begin{matrix}C^2H^4\\ (C^2H^3O)^2\end{matrix}\right\}O^2}_{\text{Diacetate of ethylene.}}$$

Monoacetate of ethylene is obtained by heating acetate of potassium with an alcoholic solution of bromide or chloride of ethylene, or by heating in a sealed tube a mixture of 1 at. hydrate of ethylene and 1 at. acetic anhydride:

$$\left.\begin{matrix}(C^2H^4)''\\ H^2\end{matrix}\right\}O^2 + (C^2H^3O)^2.O = \left.\begin{matrix}(C^2H^4)''\\ C^2H^3O.H\end{matrix}\right\}O^2 + \left.\begin{matrix}C^2H^3O\\ H\end{matrix}\right\}O$$

All these compounds when distilled with potash are converted into the corresponding diatomic alcohols. They will be more fully described in connection with these several alcohols.

3. Triatomic Acetic Ethers; Acetins. (Berthelot, Ann. Ch. Phys. [3] xli. 277; Gm. ix. 496; Gerh. iii. 950; Berthelot and De Luca, Ann. Ch. Phys. [3] liii. 433).—Compounds obtained by the union of 1 at. glycerin, $C^3H^8O^3$, with 1, 2, or 3 at. acetic acid $C^2H^4O^2$, with elimination of an equal number of atoms of water. They may be regarded as glycerin, $C^3H^5O^3.H^3$, in which 1, 2, or 3 at. hydrogen are replaced by acetyl.

Monoacetin, $C^5H^{10}O^4 = C^3H^5O^3.H^2.C^2H^3O$, is produced by heating a mixture of glycerin and glacial acetic acid to 100° for 24 hours. Slight traces are also formed by mere contact of the liquids at ordinary temperatures. It is a neutral liquid, having a slightly ethereal odour. Sp. gr. 1·20. Mixed with half its bulk of water, it forms a clear liquid, which becomes turbid on the addition of two or more volumes of water; but the acetin does not separate from it, and the emulsion continues opalescent even after the addition of a large quantity of water. Treated with alcohol and hydrochloric acid, it forms glycerin and acetate of ethyl. It mixes with ether.

Diacetin, also called *Acetidin*, $C^7H^{12}O^5 = C^3H^5O^3.H.(C^2H^3O)^2 = C^3H^8O^3 + 2C^2H^4O^2 - 2H^2O$, is obtained by heating glacial acetic acid with excess of glycerin to 200° for 3 hours; by heating the same two liquids together at 275°; by heating glycerin to 200° with acetic acid diluted with an equal bulk of water; and by heating to 200° a mixture of 1 pt. of glycerin with 4 or 5 pts. of acetic acid. It is a neutral odoriferous liquid having a sharp taste; sp. gr. about 1·85. Boils at 280°, and distils without alteration. Assumes a viscid consistency at $-40°$. It becomes slightly acid by prolonged contact with air. 100 pts. of it saponified with baryta, yield 52·4 pts. of glycerin and a quantity of acetate of barium corresponding to 66·4 pts. of acetic acid; calculation requires 52·3 glycerin and 68·2 acetic acid. With alcohol and hydrochloric acid it yields glycerin and acetate of ethyl. It dissolves in ether and in benzol.

Triacetin, $C^9H^{14}O^6 = C^3H^5O^3.(C^2H^3O)^3 = C^3H^8O^3 + 3C^2H^4O^2 - 3\,H^2O$. — Obtained by heating diacetin to 250° for 3 hours with 15 to 20 times its weight of glacial acetic acid. Resembles the preceding compound. Sp. gr. 1·174 at 8°. Volatilises without residue. 100 pts. saponified with baryta yielded 80·6 pts. acetic acid, and 43·1 glycerin; by calculation it should be 82·6 acetic acid and 42·2 glycerin. It is insoluble in water, but soluble in dilute alcohol.

A compound of acetic acid and glycerin, probably triacetin, appears to exist in cod-liver oil (De Jongh, Berz. Jahresber. 1843), and in considerable quantity in the oil obtained from the seeds of *Euonymus europæus* (Schweizer, J. pr. Chem. liii. 437). Acetic acid was also observed by Chevreul among the product of the saponification of fats.

Acetochlorhydrin, $C^5H^9ClO^3 = C^3H^8O^3 + C^2H^4O^2 + HCl - 2H^2O$, is obtained by passing hydrochloric acid gas to saturation into a mixture of acetic acid and glycerin heated to 100°, and saturating the liquid with carbonate of sodium, after leaving it at rest for several days. This process yields the compound mixed with dichlorhydrin. It is also obtained, together with the following compound, by the action of chloride of acetyl on glycerin. It is a neutral oil, smelling like acetate of ethyl and volatilising at about 250°.

Acetodichlorhydrin, $C^5H^8Cl^2O^2 = C^3H^8O^3 + C^2H^4O^2 + 2HCl - 3H^2O$, is obtained by adding chloride of acetyl to glycerin externally cooled, as long as any action takes place, distilling the product, and purifying the distillate obtained between 180° and 160°, by agitation with water and then with an alkali, drying with chloride of calcium and quicklime, and fractional rectification. It is a transparent neutral oil having a refreshing ethereal odour, sparingly soluble in water and distilling at 205° without decomposition. (Berthelot and De Luca.)

Diacetochlorhydrin, $C^7H^{11}ClO^4 = C^3H^8O^3 + 2C^2H^4O^2 + HCl - 3H^2O$, is obtained by the action of chloride of acetyl on a mixture of equal volumes of glycerin and glacial acetic acid. It is a neutral liquid which volatilises at 245°. (Berthelot and De Luca.)

Similar compounds are produced by the action of bromide of acetyl on glycerin. By treating glycerin with a mixture of chloride and bromide of acetyl in equal numbers of atoms, *acetochlorbromhydrin*, $C^5H^8ClBrO^2 = C^3H^8O^3 + C^2H^4O^2 + HCl + HBr - 3\,H^2O$, is obtained as a neutral colourless liquid, smelling like acetate of ethyl and bromide of ethylene, boiling at 208°, and distilling without decomposition. It is somewhat coloured by exposure to light. (Berthelot and De Luca.)

The formulæ of all these compounds may be derived from that of a triple molecule of water $\begin{matrix}HHO\\HHO.\\HHO\end{matrix}$ By replacing 3 at. hydrogen in this formula by the triatomic radicle, *glyceryl* C^3H^5, we obtain glycerin $\begin{array}{ll}H & O\\ H(C^3H^5) & O.\\ H & O\end{array}$ Replacing 1, 2 or 3 at. H in this formula by acetyl ($C^2H^3O = Ac$), we obtain monoacetin, &c.; and, lastly, the replacement of one or two molecules of peroxide of hydrogen (HO), by chlorine in the formulæ of monoacetin and diacetin gives the acetochlorhydrins. Thus:

Monacetin	$\begin{array}{ll}H & O\\ Ac(C^3H^5)''' & O\\ H & O\end{array}$	Acetochlorbromhydrin .	$\begin{array}{ll} & Br\\ Ac(C^3H^5)''' & O\\ & Cl\end{array}$
Acetochlorhydrin . .	$\begin{array}{ll}H & O\\ Ac(C^3H^5)''' & O\\ & Cl\end{array}$	Diacetochlorhydrin . .	$\begin{array}{ll}Ac & O\\ Ac(C^3H^5)''' & O\\ & Cl\end{array}$
Acetodichlorhydrin . .	$\begin{array}{ll} & Cl\\ Ac(C^3H^5)''' & O\\ & Cl\end{array}$	Triacetin	$Ac^3(C^3H^5)'''O^3$.

ACETITE. A compound formed from acetic acid and mannite in the same manner as acetin from acetic acid and glycerin. (Berthelot, Compt. rend. xxxviii. 668.)

ACETOMETER. A hydrometer graduated for determining the strength of commercial acetic acid according to its density. (See ACETIC ACID.)

ACETONE. $C^3H^6O = C^2H^3O.CH^3$ [or $C^6H^6O^2$]. *Pyroacetic spirit*, *Essiggeist*, *Brenzessiggeist* (Gm. ix. 1; xiii. 462; Gerh. i. 700; iii. 943; iv. 906).—This compound has long been known as a product of the destructive distillation of acetates (p. 28). It is also produced by passing the vapour of acetic acid through a red-hot tube; by heating gum, sugar, tartaric acid, citric acid and other vegetable substances in contact with lime; and by heating citric acid with permaganate of potassium, or with a mixture of binoxide of manganese and dilute sulphuric acid. (Péan de St. Gilles, Compt. rend. xlvii. 555.)

$$\underbrace{C^6H^8O^7}_{\text{Citric acid.}} + O = C^3H^6O + 3CO^2 + H^2O.$$

It is prepared: 1. By distilling acetate of barium or acetate of calcium at a moderate heat, the metal then remaining in the form of carbonate:

$$2C^2H^3BaO^2 = C^3H^6O + CO^3Ba^2.$$

Acetate of barium when dry and pure, yields a perfectly colourless neutral distillate, in fact pure acetone. The calcium-salt requires a higher temperature to decompose it, and the distillate is in consequence contaminated with an empyreumatic oil, called *dumasin*, $C^{10}H^{16}O$.—2. By distilling in an iron retort or quicksilver bottle, a mixture of 2 pts. of acetate of lead and 1 pt. of pounded quicklime, rectifying the product several times over chloride of calcium, and finally distilling over the water-bath.

Acetone is a limpid, very mobile liquid, of sp. gr. 0·792 at 18° (Liebig), 0·814 at 0° (H. Kopp). It does not solidify at −15°. Boils at 56° (Dumas), at 56·3° (Kopp) under a pressure of 760 mm. Evaporates quickly, producing a considerable degree of cold. Vapour-density 2·0025 (Dumas). It has an agreeable odour, and a biting taste like that of peppermint. It is very inflammable, and burns with a white flame, without smoke.

Acetone mixes in all proportions with water, alcohol, ether, and many compound ethers. It does not dissolve potash or chloride of calcium. It dissolves many camphors, fats and resins.

Acetone forms definite compounds with the *alkaline bisulphites*. The potassium salt, $C^3H^6O + SO^3(KH)$, and the sodium-salt, $C^3H^6O + SO^3(NaH)$ crystallise in nacreous scales (Limpricht). The *ammonium-salt*, $C^3H^6O + SO^3(NH^4H,)$ is deposited on mixing an alcoholic solution of bisulphite of ammonium with acetone, in laminæ resembling cholesterin, which quickly aggregate into a heavy crystalline powder. (Städeler.)

Acetone was regarded by Kane as an alcohol, $C^3H^5.H.O$, containing the radicle C^3H^5, which he called *mesityl*. According to this view, however, the oxidation of acetone should yield products containing C^3, just as the oxidation of common alcohol, C^2H^6O yields aldehyde and acetic acid containing C^2; but no such products are obtained. A more probable view of the composition of acetone is that of Chancel, who regards it as aldehyde coupled with methylene, $C^2H^4O.CH^2$, or, which comes to the same thing, that of Gerhardt and Williamson, who regard it as aldehyde in which the basic hydrogen is replaced by methyl; $\left.\begin{matrix}C^2H^3O\\ CH^3\end{matrix}\right\}$. This view is quite in accordance with the decomposition of acetates into acetone and carbonates. For acetyl may be regarded as a compound of methyl with carbonic oxide; $[C^2H^3O = CH^3.CO.]$; and it is easy to conceive that 2 atoms of acetate of barium $\left.\begin{matrix}CH^3.CO\\ Ba\end{matrix}\right\}O$, may decompose in such a manner that the CO of the one may unite with the two atoms of barium and the two external atoms of oxygen, to form carbonate of barium, while the methyl remains in combination with the other atom of acetyl, forming acetone:

$$\underbrace{2\left(\left.\begin{matrix}CH^3.CO\\ Ba\end{matrix}\right\}O\right)}_{\text{Acetate of barium.}} = \underbrace{\left.\begin{matrix}CO\\ Ba^2\end{matrix}\right\}O^2}_{\text{Carbonate of barium.}} + \underbrace{\left.\begin{matrix}CH^3.CO\\ CH^3\end{matrix}\right\}}_{\text{Acetone.}}$$

The same view is strengthened by the fact (discovered by Williamson) that when a mixture of acetate and valerate of barium is heated, an acetone is formed containing acetyl coupled with tetryl (C^4H^9), or valyl (C^5H^9O) with methyl: thus

$$\left.\begin{matrix}CH^3.CO\\ Ba\end{matrix}\right\}O + \left.\begin{matrix}C^4H^9.CO\\ Ba\end{matrix}\right\}O = \left.\begin{matrix}CO\\ Ba^2\end{matrix}\right\}O^2 + \left.\begin{matrix}C^2H^3O\\ C^4H^9\end{matrix}\right\}$$

Decompositions of Acetone.—1. Acetone passed in the state of vapour through a red-hot tube, deposits charcoal and is converted into a peculiar oil called *dumasin*, which generally passes over together with acetone in the distillation of acetates.

2. Acetone is decomposed by *chlorine*, a portion of its hydrogen being replaced by that element; but it is not possible in this manner to replace the whole of the hydrogen by chlorine; even a mixture of chlorate of potassium and hydrochloric acid does not appear to be capable of replacing more than two of the hydrogen atoms by chlorine. The higher chlorinated acetones, may however be obtained by the action of chlorine, or the mixture just mentioned, on other organic bodies. (See CHLORACETONES, p. 29.)

Chlorine, in presence of alkalis, converts acetone into chloroform:

$$C^3H^6O + 12\,Cl + H^2O = 2CHCl^3 + CO^2 + 6\,HCl.$$

Bromine, in presence of alkalis, acts in a similar manner, producing bromoform: but iodine forms only a dark pitchy mass.

4. *Hydrochloric acid gas* is absorbed in large quantity by acetone, and according to Kane, yields chloride of mesityl (or chloropropylene) C^3H^5Cl. *Hydriodic acid gas* passed into acetone forms, according to Kane, iodide of mesityl, C^3H^5I, which distils over with the hydriodic acid; iodide of pteleyl C^3H^3I (or rather tri-iodomesitylene, $C^9H^9I^3$), which remains suspended in the residual liquid, in the form of yellow scales; and mesityl-hypophosphorous acid, $C^3H^6O.PHO$, which separates in silky needles as the liquid cools. Friedel (Compt. rend. xlv. 1013) stated that a solution of hydrochloric acid gas in acetone yielded, when heated to 100°, acetic acid and chloride of methyl ($2C^3H^6O + 4HCl = C^2H^4O^2 + 4CH^3Cl$), and similarly with hydriodic acid; but he has since admitted that these results were obtained with impure acetone containing wood-spirit.

5. With *pentachloride of phosphorus*, acetone yields chloropropylene, C^3H^5Cl, boiling at about 30° and *methylchloracetol*, a compound isomeric with chloride of propylene, $C^3H^6Cl^2$. This body treated with silver-salts, ammonia, ethylate of sodium, or alcoholic potash, is resolved into hydrochloric acid and chloropropylene, identical with the body obtained by the action of alcoholic potash on $C^3H^6Cl^2$. Hence it appears that acetone is related to the propylene series. (Friedel, Ann. Ch. Pharm. cxii. 236.)

6. Strong *nitric acid* acts violently on acetone, giving off copious red fumes, and forming mesitic aldehyde, C^3H^4O, and nitrite of pteleyl, $C^3H^3NO^2$. [or rather trinitromesitylene, $C^9H^9(NO^2)^3$], together with oxalic and cyanuric acid (Kane). By dropping acetone into fuming nitric acid contained in a flask externally cooled, and adding water as soon as the action ceases, a heavy oil is obtained, which explodes with violence when heated, giving off red fumes. (Fittig, Ann. Ch. Pharm. cx. 45.)

7. Acetone mixed with strong *sulphuric acid* becomes heated, and, according to the quantity of acid present and the rise of temperature which takes place, forms either

oxide of mesityl, $C^6H^{10}O$, or mesitylene, C^9H^{12}, together with mesitylsulphuric acid, $SO^4.C^3H^5.H$, and sulphurous acid. (According to Kane, the composition of mesitylsulphuric acid is $C^6H^5O.HO.SO^3$, and there is formed at the same time another acid called *permesitylsulphuric* acid, $C^6H^5O^2.\ 2\,SO^4H$).

8. Glacial *phosphoric* acid forms with acetone a dark brown mass, partly consisting of mesitylphosphoric acid. (Kane.)

9. A solution of *phosphorus* in acetone turns acid when kept for some weeks, and more quickly when heated, even in perfectly air-tight vessels. According to Zeise, the change consists in the formation of three peculiar acids, to which he gives the names, *phosphacetic, acephosgenic* and *acephoric* acids; but their nature and composition have not been clearly made out. Products of like nature are obtained with *sulphur*. *Sulphide of phosphorus* forms with acetone a peculiar acid, and an oil which has a powerful odour but no acid reaction. (Zeise.)

10. A solution of *ammonia* in acetone yields, by spontaneous evaporation, a colourless syrupy residue, which gradually changes into an alkaline liquid, consisting of *acetonine*, $C^9H^{18}N^2$, an organic base, which bears to acetone the same relation that amarine bears to bitter-almond oil:

$$3C^3H^6O + 2\,NH^3 = C^9H^{18}N^2 + 3H^2O.$$

The non-basic compound first formed is perhaps isomeric with acetonine. (Städeler, Chem. Gaz. 1853, 241.)

11. By the action of *ammonia* and *sulphur* on acetone, Zeise obtained a number of products, which however do not present any definite characters. (Gm. ix. 11.)

12. By the simultaneous action of *ammonia* and *hydrosulphuric acid*, acetone is converted into *thiacetonine*, a sulphuretted base consisting probably of $C^9H^9NS^2$. It crystallises in shining yellowish rhombohedrons, having an alkaline reaction, sparingly soluble in water, but dissolving with facility in alcohol, ether, acetone, and dilute acids. (Städeler.)

13. When 1 volume of acetone is mixed with 1 vol. *disulphide of carbon* and 2 vols. aqueous *ammonia*, laminated crystals, resembling ice, form in the liquid after a few days; but these gradually disappear, and are succeeded by large yellow crystals, which are insoluble in water, sparingly soluble in ether, but dissolve, with decomposition, in warm alcohol and in boiling hydrochloric acid (Hlasiwetz, J. pr. Chem. li. 355). Hlasiwetz assigns to these crystals the improbable formula $C^{30}H^{32}N^6S^9$. Städeler, on the other hand, regards them as the hydrosulphate of an organic base, *carbothiacetonine*, $C^{10}H^{18}N^2S^2$, and represents their formation by the equation,

$$3\,C^3H^6O + 2NH^3 + CS^2 = C^{10}H^{18}N^2S^2 + 3H^2O.$$

The formula $C^{10}H^{18}N^2S^2.H^2S$ agrees pretty nearly with the analytical numbers obtained by Hlasiwetz. A cold alcoholic solution of the crystals forms with dichloride of platinum a brownish yellow, amorphous precipitate consisting of $C^{10}H^{18}N^2S^2.PtCl^2.PtS$, and with mercuric chloride a white precipitate, which, according to Städeler, is merely Hg^2Cl^2S mixed with a small quantity of hydrochlorate of carbothiacetonine.

14. Acetone heated with a mixture of *hydrocyanic* and *hydrochloric acid*, is converted into *acetonic acid*, $C^4H^8O^3$ (Städeler):

$$C^3H^6O + CNH + 2\,H^2O = C^4H^8O^3 + NH^3.$$

15. Acetone distilled with *dichromate of potassium* and *sulphuric acid*, gives off acetic and carbonic acids, but no formic acid:

$$C^3H^6O + 4O = C^2H^4O^2 + CO^2 + H^2O.$$

16. Caustic alkalis, such as *hydrate of potassium* and *quick lime*, exert a dehydrating action on acetone, several products being formed, according to the proportion of water abstracted. Löwig and Weidmann, by subjecting acetone to the action of hydrate of potassium, obtained a dark brown mass, consisting chiefly of *xylite-oil*, $C^{12}H^{18}O$, which boiled at 200°, together with a resin which they call *xylite-resin*. Völckel, by leaving acetone for some time in contact with quick lime, also obtained an oil boiling above 200°, which he regarded as xylite-oil. But, according to Fittig (Ann. Ch. Pharm. cx. 32), the products obtained by the action of quick lime in closed vessels, are oxide of mesityl, $C^6H^{10}O^2$, boiling at 131°, and a liquid isomeric or identical with *phorone*, $C^9H^{14}O$. It must also be noticed that Schweizer and Weidmann (J. pr. Chem. xxiii. 14) obtained xylite-oil, and likewise xylite-naphtha, $C^{12}H^{22}O^3$, by the action of potash and of strong sulphuric acid on a compound produced from crude wood-spirit, which those chemists called *xylite*, assigning to it the improbable formula $C^6H^6O^{2\frac{1}{2}}$, but which was probably nothing but somewhat impure acetone. On the whole it appears that the action of alkalis on acetone is similar to that of sulphuric acid (p. 52), consisting in an abstraction of the elements of water. The products

obtained by the action of these dehydrating agents on acetone may be arranged as follows, according to their boiling-points:

		Boiling-point.
Xylite-naphtha . .	$C^{12}H^{22}O^{3} = 4\,C^{3}H^{6}O - H^{2}O$.	. 110° to 120°
Oxide of Mesityl .	$C^{6}H^{10}O = 2\,C^{3}H^{6}O - H^{2}O$.	. „ 131°
Mesitylene . .	$C^{9}H^{12} = 3\,C^{3}H^{6}O - 3H^{2}O$.	. 155° „ 160°
Phorone? . .	$C^{9}H^{14}O = 3\,C^{3}H^{6}O - 2H^{2}O$.	. 210° „ 220°
Xylite-oil . .	$C^{12}H^{18}O = 4\,C^{3}H^{6}O - 3H^{2}O$.	. above 200°

Vapour of acetone passed over heated hydrate of potassium or potash-lime is resolved into marsh-gas and carbonic anhydride:

$$C^{3}H^{6}O + 2\,KHO = CO^{3}K^{2} + 2\,CH^{4};$$

or if the heat is not very strong, the chief products are acetic acid, formic acid and hydrogen:

$$C^{3}H^{6}O + 2\,KHO + H^{2}O = C^{2}H^{3}KO^{2} + CHKO^{2} + 6\,H.$$

17. *Sodium* is violently attacked by anhydrous acetone, but without evolution of hydrogen, and hydrate of sodium is separated in white flakes. The liquid gradually assumes a pasty consistence, and the sodium becomes coated with oxide, so that it no longer acts perceptibly on the acetone. On distilling the mass, undecomposed acetone passes over first, and afterwards a watery liquid collects in the receiver, covered with a yellowish oil. On pouring the distillate into a basin, so that the undecomposed acetone may evaporate, the watery layer solidifies in a white crystalline mass, from which the oil may be separated by pressure between paper. The crystals consist of *hydrate of pinacone*, $C^{6}H^{12}O + 7\,H^{2}O$, and the oily liquid is *phorone*, $C^{9}H^{14}O$. The pinacone is produced by the abstraction of 1 at. oxygen from a double molecule of acetone:

$$2\,C^{3}H^{6}O + 2\,Na = Na^{2}O + C^{6}H^{12}O;$$

and the anhydrous pinacone thus formed appears to take water from another portion of the acetone, converting it into phorone:

$$3\,C^{3}H^{6}O - 2\,H^{2}O = C^{9}H^{14}O.$$

By heating the crystals of hydrated pinacone in a narrow glass tube, a viscid liquid is obtained, which absorbs water rapidly from the air, and is reconverted into the crystalline hydrate. This liquid appears to be anhydrous pinacone; but it is difficult to expel all the water (Städeler, Ann. Ch. Pharm. cxi. 277). Fittig (ibid. cx. 23) assigns to the hydrated crystals, the formula $C^{3}H^{6}O + 3H^{2}O$, regarding them as the hydrate of *paracetone*, a compound isomeric with acetone, which he also states is obtained in anhydrous crystals, by the action of ammonia on acetone. Fittig's formulæ do not, however, agree with the results of analysis so well as Städeler's (see PINACONE); moreover it is very unlikely that sodium should act with violence on acetone, without abstracting a portion of its oxygen. The action of ammonia on acetone, produces, according to Städeler, not a crystalline compound, but a liquid organic base, acetonine (p. 32).

18. Dry *dichloride of platinum* dissolves in acetone with evolution of heat, and forms a brown solution, which, when evaporated, gives off hydrochloric acid, and leaves a resinous mass, containing among other products, a yellow crystalline substance called *acechloride of platinum* or *chloroplatinite of mesityl*, $C^{6}H^{10}O.Pt^{2}Cl^{2}$. (?) This compound may be obtained in larger quantity, by triturating dichloride of platinum with acetone to the consistence of a thick paste, leaving the mass in a close vessel till it liquefies and ultimately forms crystals, washing these crystals with acetone, and purifying them by crystallisation from boiling acetone. Acechloride of platinum thus obtained, is yellow, inodorous, sparingly soluble in water, alcohol and ether, more readily in aqueous chloride of potassium or sodium. Cold acetone dissolves $\frac{1}{80}$ of it; boiling acetone a little more. The aqueous solution reddens litmus. The compound is decomposed and dissolved by potash, forming a brown solution. When boiled with water, it deposits a black substance called *aceplatinous oxide*, probably $C^{2}Pt^{2}O$. The same substance is deposited on boiling the mother-liquor of acichloride of platinum. The acichloride yields by distillation a residue of carbide of platinum, PtC. (Zeise, Ann. Ch. Pharm. xxxiii. 29; Gm. ix. 31.)

SUBSTITUTION-PRODUCTS OF ACETONE. *Chloracetones.*—Each of the atoms of hydrogen in acetone may be replaced by chlorine, giving rise to six chlorinated acetones. The first of these compounds is obtained by the action of nascent chlorine on acetone; the second by that of chlorine or the oxides of chlorine on acetone; the third and fourth by the action of chlorine on crude wood-spirit, probably containing acetone; the fifth and sixth can only be obtained by the action of chlorine or the oxides of chlorine on other organic compounds.

Monochloracetone, C^3H^5ClO, is obtained by the action of a feeble electric current (from three Bunsen's cells) on a mixture of acetone and hydrochloric acid, the chlorine set free at the positive pole from the hydrochloric acid, acting on the acetone and taking the place of 1 at. hydrogen. It is an oily, colourless liquid, which, when separated from the watery solution and rectified, boils at 117°, has a sp. gr. of 1·14 at 14°, and vapour-density = 3·40. Its vapour acts strongly on the nose and eyes, producing a copious flow of tears. (Riche, Compt. rend. xlix. 176.)

Dichloracetone, $C^3H^4Cl^2O$ (Kane's *mesitic chloral*), is produced by passing dry chlorine into anhydrous acetone, or better, according to Städeler, by mixing acetone in a capacious flask with twice its volume of strong hydrochloric acid diluted with an equal bulk of water, and adding pulverized chlorate of potassium by small portions. It is an oily liquid of sp. gr. 1·331 (Kane); 1·236 at 90° (Fittig). Boils at 116·5° (Städeler); at 121°·5 (Fittig). Vapour-density 3·2. Its vapour smells like chloroform at first, but, after a few seconds, attacks the nose and eyes with violence. The liquid blisters the skin like cantharides, producing wounds which are difficult to heal (Liebig, Kane, Fittig.) It is insoluble in water, but mixes in all proportions with alcohol and ether.

Trichloracetone, $C^3H^3Cl^3O$, is obtained by the action of chlorine on wood-spirit. When chlorine gas is passed into ordinary (unpurified) wood-spirit, crystals are formed consisting of $C^5H^{10}Cl^2O^2$ (*chloromesitate of methylene*), but if the action of the chlorine be further continued, the crystals disappear, and an oily liquid is formed, which is terchlorinated acetone. It is heavier than water, has an extremely pungent odour, and cannot be distilled without decomposition. (Bouis.)

Tetrachloracetone, $C^3H^2Cl^4O$, is obtained by dissolving the crystals just mentioned in wood-spirit and passing chlorine through the solution. It is an oily very volatile and pungent liquid, which blisters the skin. When exposed to moist air, it forms crystals containing $C^3H^2Cl^4O + 4\,H^2O$, which melt at 35°, and dissolve in water, alcohol and ether, forming solutions which are not precipitated by nitrate of silver. The crystals distilled with phosphoric anhydride yield the original anhydrous compound. This and the preceding compound are doubtless formed from acetone contained in the wood-spirit. (Bouis, Ann. Ch. Phys. [3] xxi. 111.)

Pentachloracetone, C^3HCl^5O, is obtained by the action of a mixture of chlorate of potassium and hydrochloric acid on several organic compounds, viz. kinic, citric, gallic, pyrogallic, catechucic and salicylic acids, also kinone, muscular flesh, albumin, indigo and tyrosin. The best mode of preparing it is to add a considerable quantity of chlorate of potassium to a boiling solution of kinic acid, and then add strong hydrochloric acid in such portions that chlorine and chlorous acid may be continually evolved. The distillate is concentrated by rectification over chloride of calcium. It then, if tolerably pure, solidifies into a crystalline hydrate when covered with water at 4° or 5°. If no solidification takes place, the product is contaminated with other oils, and must be purified by agitating it with ice-cold water, and heating the decanted and clarified liquid to 60°; the greater part of the oily impurities then separate out. To purify it completely, it is converted into the crystalline hydrate as above mentioned, and the crystals are pressed between paper. The pure anhydrous compound may be obtained by melting the crystals in a glass tube, whereupon they separate into a watery and an oily liquid, the latter, which is undermost, being pure anhydrous pentachloracetone. It is a colourless rather mobile oil, having a burning aromatic taste, and an odour like that of chloral. Sp. gr. between 1·6 and 1·7. It remains liquid at −20° and boils at 190°. The hydrate, which crystallises in rhombic tables, contains 4 atoms of water. Water dissolves $\frac{1}{10}$ of its volume of anhydrous pentachloracetone, and on the other hand, this compound takes up a certain quantity of water without change of appearance; but it then becomes turbid at the heat of the hand, like hydrated conine. Pentachloracetone dissolves readily in alcohol and ether. The alcoholic solution mixed with alcoholic potash deposits chloride of potassium together with scaly crystals, probably consisting of *dichloracetate* of *potassium*, and the solution is found to contain formic acid:

$$C^3HCl^5O + H^2O = \underbrace{CHCl^3}_{\text{Chloroform.}} + \underbrace{C^2H^2Cl^2O^2}_{\text{Dichloracetic acid.}}$$

and:

$$CHCl^3 + 2\,H^2O = 3\,HCl + CH^2O^2.$$

(Städeler, Ann. Ch. Pharm. cxi. 277.)

Hexachloracetone, C^3Cl^6O (discovered by Plantamour, who assigned to it the formula ($C^8Cl^{10}O^3$), is obtained by the action of chlorine in sunshine on an aqueous solution of citric acid. It is an oily liquid of peculiar pungent odour, sp. gr. 1·75 at 10°, and boiling between 200° and 201°. It makes transient grease spots upon paper, gradually reddens litmus paper, and forms with water, at temperatures not above 6°, a crystalline hydrate, $C^3Cl^6O + H^2O$, which melts at a temperature above 15°, with separation of an oil.

Bromacetone, C^3H^5BrO, is produced similarly to monochloracetone, viz. by the action of a feeble electric current on a mixture of acetone and hydrobromic acid. It is colourless when first prepared, but turns brown in a few minutes, and is decomposed by distillation, the greater portion however passing over between 140° and 145°. Its vapour irritates the eyes so strongly that the spilling of a few drops renders the air of a room unendurable. (Riche.)

Iodacetone appears also to be formed in small quantity by the electrolysis of a mixture of acetone and hydriodic acid. (Riche.)

Methylacetone, $C^4H^8O = C^3H^5(CH^3)O$. — When crude commercial acetone, or, better, the brown liquid which floats on the top of it, is dehydrated with chloride of calcium and then subjected to fractional distillation, pure acetone passes over below 60° and the distillate which is obtained between 60° and 130°, yields, after about thirty fractionations, three distinct compounds, viz. methylacetone, boiling between 75° and 77°, ethylacetone, $C^5H^{10}O$, between 90°, and 95° and dumasin, $C^6H^{10}O$, between 120° and 125°. (Fittig, Ann. Ch. Pharm. cx. 18.)

Methylacetone is a colourless liquid of sp. gr. 0·838 at 19° C. having the odour of acetone, miscible in all proportions with water and alcohol. It combines with acid sulphite of sodium, forming a crystalline compound, $2C^4H^7NaSO^4 + 3H^2O$, which is very soluble in water.

Ethylacetone, $C^5H^{10}O = C^3H^5(C^2H^5)O$. — Transparent, colourless liquid, smelling faintly like acetone, sparingly soluble in water, but miscible in all proportions with alcohol, sp. gr. 0·842 at 19°. Boils between 90° and 95°. With acid sulphite of sodium it forms the compound $2C^5H^9NaSO^3 + 3H^2O$, which crystallises in colourless nacreous laminæ very soluble in water. (Fittig.)

ACETONES or KETONES. This term is applied to a class of compounds which, like that just described, are composed of an acid-radicle united with an alcohol-radicle. Nearly all the acetones at present known consist of the radicle of a fatty acid combined with one of the corresponding alcohol-radicles; their general formula being $C^mH^{2m+1}.C^nH^{2n-1}O$. where *m* may be either greater or less than *n*. When $m = 0$, the acetone becomes an aldehyde, $H.C^nH^{2n-1}O = C^nH^{2n}O$; the acetones may therefore be regarded as aldehydes in which 1 at. hydrogen is replaced by an alcohol-radicle.

Acetones are either *simple* or *compound*. In the simple acetones, $m = n - 1$, so that their general formula is $C^{n-1}H^{2n-1}.C^nH^{2n-1}O. = C^{2n-1}H^{4n-2}O$; thus, acetic acetone, for which $n = 2$, is $CH^3.C^2H^3O$. The simple acetones are produced by heating the barium or calcium salts of the fatty acids, 2 atoms of the salt being decomposed in such a manner that the acid radicle of one of them is resolved into the next lowest alcohol-radicle and carbonyl (CO), so that a carbonate of calcium or barium is formed at the same time:

$$\left.\begin{matrix} C^nH^{2n-1}O \\ Ca \end{matrix}\right\}O + \left.\begin{matrix} CO.C^{n-1}H^{2n-1} \\ Ca \end{matrix}\right\}O = \left.\begin{matrix} C^nH^{2n-1}O \\ C^{n-1}H^{2n-1} \end{matrix}\right\} + \left.\begin{matrix} CO \\ Ca^2 \end{matrix}\right\}O^2.$$

The formation of acetic acetone or methyl-acetyl (p. 26) by the decomposition of acetate of barium, is a particular example of this process. In like manner, *propione* or *ethyl-propionyl*, $C^2H^5.C^3H^5O$, *butyrone* or *trityl-butyryl*, $C^3H^7.C^4H^7O$, *valerone* or *tetryl-valyl*, $C^4H^9.C^5H^9O$, are produced by the decomposition of the propionates, butyrates valerates, &c.

These simple acetones were the only ones known, till Williamson in 1851 (Chem. Soc. Qu. J. iv. 238) showed that, by distilling a mixture of the barium or calcium salts of two different fatty acids, acetones may be obtained in which an acid radicle is associated with an alcohol-radicle which is not the next below it in the series [*m* greater or less than $n-1$]: these are the so-called compound or intermediate acetones. If the acids whose salts are distilled together contain *p* and *q* atoms of carbon, the decomposition may be represented by the equation:

$$\left.\begin{matrix} C^pH^{2p-1}O \\ Ca \end{matrix}\right\}O + \left.\begin{matrix} CO.C^{q-1}H^{2q-1} \\ Ca \end{matrix}\right\}O = \left.\begin{matrix} C^pH^{2p-1}O \\ C^{q-1}H^{2q-1} \end{matrix}\right\} + \left.\begin{matrix} CO \\ Ca^2 \end{matrix}\right\}O^2.$$

or, since it is indifferent which of the acid radicles we suppose to be decomposed, the formula of the acetone thus produced may also be $\left.\begin{matrix} C^qH^{2q-1}O \\ C^{p-1}H^{2p-1} \end{matrix}\right\}$. Thus a mixture of acetate and valerate of calcium yields by distillation either *methyl-valyl*, $CH^3.C^5H^9O$, or *tetryl-acetyl*, $C^4H^9.C^2H^3O$, either of these formulæ being equal to $C^6H^{12}O$. Possibly two isomeric compounds having these formulæ, may be produced together. If one of the mixed salts is a formate, $\left.\begin{matrix} CO.H \\ Ca \end{matrix}\right\}O$, the alcohol-radicle separated from it is reduced to an atom of hydrogen, and the acetone becomes an aldehyde. (See ALDEHYDES.)

The compound acetones are also produced, together with the simple acetones and other products, when a calcium or barium salt of a fatty acid is distilled alone. Thus the distillation of butyrate of calcium yields, besides butyrone and a small quantity of butyral, a considerable number of hydrocarbons (Berthelot, Compt. rend. xliii. 236); and among these, methyl and ethyl appear to occur, and give rise to the formation of *ethyl-butyryl*, $C^2H^5.C^4H^7O$, and *methyl-butyryl*, $CH^3.C^4H^7O$. (Friedel, Compt. rend, xlvii. 553.)

The following is a list of the acetones, or ketones, at present known, which are derived from the fatty acids:

Methyl-acetyl (Acetone)	$C^3H^6O = CH^3 . C^2H^3O$
Methyl-butyryl	$C^5H^{10}O = CH^3 . C^4H^7O$
Ethyl-propionyl (Propione) . . .	$C^5H^{10}O = C^2H^5 . C^3H^5O$
Ethyl-butyryl	$C^6H^{12}O = C^2H^5 . C^4H^7O$
Methyl-valyl	$C^6H^{12}O = C\ H^3 . C^5H^9O$
Trityl-butyryl (Butyrone)	$C^7H^{14}O = C^3H^7 . C^4H^7O$
Methyl-œnanthyl	$C^8H^{16}O = C\ H^3 . C^7H^{13}O$
Tetryl-valyl (Valerone)	$C^9H^{18}O = C^4H^9 . C^5H^9O$
Amyl-capronyl (Capronone) . . .	$C^{11}H^{22}O = C^5H^{11} . C^6H^{11}O$
Heptyl-capryl (Caprylone) . . .	$C^{15}H^{30}O = C^7H^{15} . C^8H^{15}O$
Octyl-pelargonyl (Pelargonone) . .	$C^{17}H^{34}O = C^8H^{17} . C^9H^{17}O$
Laurone	$C^{23}H^{46}O = C^{11}H^{23} . C^{12}H^{23}O$
Myristone	$C^{27}H^{54}C = C^{13}H^{27} . C^{14}H^{27}O$
Palmitone or Margarone	$C^{31}H^{62}O = C^{15}H^{31} . C^{16}H^{31}O$
Stearone	$C^{35}H^{70}O = C^{17}H^{35} . C^{18}H^{35}O$

Some of the compounds in this table are isomeric, *e. g.* propione and butyracetone. Among the higher terms of the series, the number of such isomeric compounds is doubtless very great, though but few of them have yet been obtained.

These bodies, with the exception of acetic acetone, have not been much studied. Their reactions, so far as they are known, resemble those of common acetone already described. The lower terms of the series unite with the acid sulphites of the alkali-metals, generally forming crystalline compounds. The best mode of purifying the acetones is to shake them up with a strong aqueous solution of acid sulphite of potassium or sodium, and distil the resulting solid compound with potash. The acetone then passes over pure.

But little is known respecting acetones belonging to other series of acids. Two have been formed containing the radicle benzoyl, viz. *benzophenone*, or *phenyl-benzoyl*, $C^{13}H^{10}O = C^6H^5.C^7H^5O$, the acetone of benzoic acid, obtained by heating benzoate of potassium; and *methyl-benzoyl*, $C^8H^8O = CH^3.C^7H^5O$, obtained by distilling together equivalent quantities of acetate and benzoate of calcium (Friedel). Benzophenone treated with nitric acid yields *nitrobenzophenone*, $C^{13}H^8(NO^2)^2O$.

The calcium-salt of camphoric acid, which is dibasic, yields by dry distillation an oily liquid called *phorone*, which has the constitution of an acetone:

$$\underbrace{\left.\begin{matrix}C^{10}H^{14}O^2\\ Ca^2\end{matrix}\right\}}_{\text{Camphorate of calcium.}} O^2 = \underbrace{C^9H^{14}O}_{\text{Phorone.}} + \underbrace{\left.\begin{matrix}CO\\ Ca^2\end{matrix}\right\}}_{\text{Carbonate of calcium.}} O^2;$$

and suberate of calcium, $C^8H^{12}O^4Ca^2$, yields in like manner *suberone*, $C^7H^{14}O$, mixed with other products. These are the only two acetones of dibasic acids yet discovered. (Gerhardt, Traité, iv. 640.)

ACETONINE. $C^9H^{18}N^2$.—Produced by the action of ammonia on acetone (p. 28), either when a solution of ammonia in acetone is left to evaporate spontaneously to a syrup, or when acetone saturated with ammonia is heated to 100° in a sealed tube. It is a colourless liquid, having a peculiar urinous odour, a burning taste and alkaline reaction, easily soluble in water, alcohol, and ether. It unites with acids, forming salts. The *oxalate* $C^9H^{18}N^2.C^2H^2O^4 + H^2O$ crystallises from a hot saturated alcoholic solution in delicate colourless prisms, which are soluble in water, insoluble in ether, give off half their water at 100°, the rest between 115° and 120°, and decompose at a higher temperature. The *chloroplatinate*, $C^9H^{18}N^2.HCl.PtCl^2$, forms lustrous, orange-coloured, four-sided prisms with oblique terminal faces. It is soluble in water, also in boiling alcohol containing hydrochloric acid; insoluble in ether. (Städeler, Ann. Ch. Pharm. cxi. 308.)

ACETONITRILE. C^2H^3N.—A compound obtained by treating acetate of ammonium or acetamide with phosphoric anhydride:

$$\underbrace{C^2H^3O^2.NH^4}_{\text{Acetate of ammonium.}} - 2H^2O = C^2H^3N;\ \text{and}\ \underbrace{C^2H^5NO}_{\text{Acetamide.}} - H^2O = C^2H^3N.$$

It is identical with cyanide of methyl, obtained by distilling cyanide of potassium with methylsulphate of potassium. (See CYANIDE OF METHYL.)

Chloracetonitrile, C^2Cl^3N, or cyanide of trichloromethyl, $CCl^3.CN$, is obtained by distilling trichloracetate of ammonium or trichloracetamide with phosphoric anhydride. It is a liquid boiling at 81°; of sp. gr. 1·4441. With boiling potash, it yields ammonia and trichloracetate of potassium. It is violently attacked by potassium.

ACETONYL. C^6H^{12}.—A hypothetical radicle supposed by Hlasiwetz to exist in the yellow crystals formed by the action of ammonia and bisulphide of carbon on acetone. Hlasiwetz assigns to these crystals the formula $C^{30}H^{52}N^6S^8$, and regards them as *sulphocyanate of acetonyl with sulphocarbonate of sulphacetonyl* = $2(C^6H^{12}.2CNS) + 2C^6H^{12}S.C^2H^4N^2S^2$. Städeler's view of the constitution of this compound (p. 52), is much more probable.

ACETOSYL. The name given by Gerhardt to the hypothetical radicle C^2H^3 or C^4H^3, originally called *acetyl*, and supposed by some chemists to exist in acetic acid and its derivatives. (See ACETYL and VINYL.)

ACETOXYL. Kolbe's name for the radicle C^2H^3O or $C^4H^3O^2$, usually called acetyl, which see.

ACETUREÏD. Syn. of Acetyl-urea.

ACETYL. C^2H^3O or $C^4H^3O^2$. *Acetoxyl, Othyl.*—A radicle not yet isolated, but supposed to exist in acetic acid and its derivatives, the rational formula of acetic acid being, on this hypothesis, $\left.\begin{matrix}C^2H^3O\\H\end{matrix}\right\}O$, and that of acetic anhydride, $\left.\begin{matrix}C^2H^3O\\C^2H^3O\end{matrix}\right\}O$.

The reason for assuming the existence of this radicle in the acetic compounds is, that the formula to which it leads, affords the simplest representation of the most important reactions of acetic acid and the other bodies of the series. Thus, when acetic acid $\left.\begin{matrix}C^2H^3O\\H\end{matrix}\right\}O$ is treated with a metallic oxide or hydrate, the basic atom of hydrogen is replaced by a metal, and an acetate of that metal $\left.\begin{matrix}C^2H^3O\\M\end{matrix}\right\}O$ is produced. On treating the same compound with pentasulphide of phosphorus, P^2S^5, the external atom of oxygen is replaced by sulphur, and thiacetic acid, $\left.\begin{matrix}C^2H^3O\\H\end{matrix}\right\}S$ is formed; and by the action of pentachloride of phosphorus, the group HO is replaced by Cl, and chloride of acetyl $C^2H^3O.Cl$ is produced. (See ACETIC ACID, and ACIDS, p. 44.)

Formerly, however, acetic acid, and the other members of the same group, were supposed to be derived from the radicle C^2H^3 or C^4H^3; and to this the name *acetyl* was originally applied. Thus, anhydrous acetic acid was regarded as a trioxide of this radicle, viz. $C^4H^3.O^3$, and the hydrated acid as a compound of this oxide with water, viz. $C^4H^3O^3.HO$. &c. To apply the same name to two different radicles would of course create confusion; hence the terms *acetoxyl* proposed by Kolbe, and *othyl* (abbreviation of oxygen-ethyl) by Williamson, for the radicle C^2H^3O. Most chemists, however, are of opinion, that the radicle supposed to exist in acetic acid and its derivatives, is most appropriately designated by the term *acetyl;* and accordingly, this term is now generally applied to the group C^2H^3O, while C^2H^3, which more properly belongs to another series of compounds derived from alcohol, ether and ethylene, and having a less intimate distant relation to acetic acid, is called by a different name. (See ACETOSYL and VINYL.)

Acetyl, C^2H^3O is regarded by Kolbe as a compound or conjugate radicle, containing methyl and carbonyl, viz. CH^3,CO; and in like manner, propionyl, C^3H^5O, is regarded as a compound of ethyl: $C^2H^5.CO$; butyryl, C^4H^7O, as a compound of trityl: $C^3H^7.CO$, &c. each radicle of a fatty acid being supposed to contain the next lowest alcohol-radicle associated with carbonyl. This view, which has been adopted by Gerhardt, in his "Traité de Chimie Organique" is based upon the fact that certain methyl-compounds may be obtained from acetic acid and its derivatives, and the contrary; similar transformations likewise taking place in the other terms of the series. Thus, a solution of acetate of potassium subjected to electrolysis, yields methyl and carbonic anhydride:

$$\underbrace{\left.\begin{matrix}CH^3.CO\\H\end{matrix}\right\}O}_{\text{Acetic acid.}} = \underbrace{CH^3}_{\text{Methyl.}} + CO^2 + H$$

Cyanide of methyl boiled with aqueous potash gives off ammonia and forms acetate of potassium:

$$\underbrace{CH^3.CN}_{\text{Cyanide of methyl}} + KHO + H^2O = \underbrace{\left.\begin{matrix}CH^3.CO\\K\end{matrix}\right\}}_{\text{Acetate of potassium.}}O + NH^3;$$

and acetate of ammonium $(CH^3.CO).NH^4.O$, treated with phosphoric anhydride, gives off $2H^2O$, and is reduced to cyanide of methyl, $CH^3.CN$. Marsh-gas, or hydride of methyl, $CH^3.H$, is produced by the decomposition of acetates (p. 12); and cacodyl $As(CH^3)^2$, by the decomposition of acetic acid. The formation of acetone or methyl-acetyl, $CH^3.C^2H^3O$, from acetates, and the corresponding transformations of propionates, valerates, &c. (p. 26), is another example of the same kind of decomposition. Again it has been shown by Wanklyn (Chem. Soc. Q. J. xi. 103), that sodium-ethyl subjected to the action of carbonic anhydride is converted into propionate of sodium:

$$\underbrace{C^2H^5.Na}_{\text{Sodium-ethyl.}} + CO^2 = \underbrace{(C^2H^5.CO).Na.O}_{\text{Propionate of sodium.}};$$

and in like manner, acetate of sodium may be prepared from sodium-methyl. Lastly, many organic compounds, such as sugar, starch, alcohol, and acetone, which are convertible into acetic acid by oxidation, may also, under the influence of chlorine, or bromine, be converted into bodies belonging to the methyl-series, viz. chloroform, $C(HCl^2).Cl$, and bromoform, $C(HBr^2).Br$. It must be observed, however, that the representation of acetic acid as a methyl-compound applies chiefly to a state of transition, just as the acid is being produced from or converted into a body belonging to a different series, and exhibiting different chemical relations; so long as we are concerned with the transformation of one acetyl-compound into another, such as that of acetic acid into chloride or bromide of acetyl, or of the chloride into acetic anhydride, the formula $\left.\begin{matrix}C^2H^3O\\H\end{matrix}\right\}O$ is sufficient for the representation of all the changes which take place.

The hydrogen in acetyl may be partly or wholly replaced by other elements, viz. chlorine, bromine, &c.; and hence arise the conjugate or derivative radicles, *bromacetyl*, *chloracetyl*, &c., which, like acetyl itself, are hypothetical, not having yet been isolated. The following table exhibits a general view of the compounds of acetyl and of the radicles derived from it by substitution.

Bromide of Acetyl	$C^2H^3O.Br$	
Chloride	$C^2H^3O.Cl$	
Iodide	$C^2H^3O.I$	
Hydride	$C^2H^3O.H$	Aldehyde
Hydrate	$C^2H^3O.H.O$	Acetic acid
Oxide	$(C^2H^3O)^2.O$	Acetic anhydride
Peroxide	$C^2H^3O.O$	
Sulphydrate	$C^2H^3O.H.S$	Thiacetic acid
Sulphide	$(C^2H^3O)^2.S$	Thiacetic anhydride
Nitrides	$C^2H^3O.H^2.N$	Acetamide
	$(C^2H^3O)^2.H.N$	Diacetamide
	$C^2H^3O.C^2H^5.H.N$	Ethyl-acetamide
	&c.	&c.
Hydrate of Bromacetyl	$C^2H^2BrO.H.O$	Bromacetic acid
Nitride	$C^2H^2BrO.H^2.N$	Bromacetamide
Hydrate of Dibromacetyl	$C^2HBr^2O.H.O$	Dibromacetic acid
Nitride	$C^2HBr^2O.H^2.N$	Dibromacetamide
Hydride of Tribromacetyl	$C^2Br^3O.H$	Bromal
Hydrate of Chloracetyl	$C^2H^2ClO.H.O$	Chloracetic acid
Nitride	$C^2H^2ClO.H^2.N$	Chloracetamide
Chloride of Trichloracetyl	$C^2Cl^3O.Cl$	Chloraldehyde
Hydride	$C^2Cl^3O.H$	Chloral
Hydrate	$C^2Cl^3O.H.O$	Trichloracetic acid
Nitride	$C^2Cl^3O.H^2.N.$	Trichloracetamide
Phosphide	$C^2Cl^3O.H^2.P.$	Trichloracetyphide
Hydrate of Iodacetyl	$C^2H^2IO.H.O$	Iodacetic acid
Nitride	$C^2H^2IO.H^2.N$	Iodacetamide
Hydrate of Di-iodacetyl	$C^2HI^2O.H.O$	Di-iodacetic acid
Nitride	$C^2HI^2O.H^2.N.$	Di-iodacetamide
Hydride of Tri-iodacetyl	$C^2I^3O.H.$	Iodal

Bromide of Acetyl. $C^2H^3O.Br$.—Prepared by slowly adding glacial acetic acid to pentabromide of phosphorus in a tubulated retort, distilling, and rectifying:

$$C^2H^3O.H.O + PBr^3.Br^2 = C^2H^3O.Br + HBr + PBr^3O.$$

It is a colourless liquid, boiling at 81°. When exposed to the air, it fumes strongly and immediately turns yellow. It colours the skin yellow, and is said to impart to it the odour of phosphuretted hydrogen; but this must arise from impurity. Water decomposes it into acetic and hydrobromic acids. (**Ritter**, Ann. Ch. Pharm. xcv. 209.)

Chloride of Acetyl. $C^2H^3O.Cl$.—Produced by the action of oxychloride of phosphorus on acetate of potassium:

$$3(C^2H^3O.K.O) + POCl^3 = 3C^2H^3OCl + PO^4K^3;$$

or in the same manner as the preceding compound, by distilling glacial acetic acid with pentachloride of phosphorus:

$$C^2H^3O.H.O + PCl^3.Cl^2. = C^2H^3O.Cl + HCl + PCl^3O.$$

Gerhardt, who discovered this compound (Ann. Ch. Phys. [3] xxxvii. 294), prepared it by adding oxychloride of phosphorus, drop by drop, to fused acetate of potassium. A brisk action then takes place, and sufficient heat is produced to cause the chloride of acetyl to distil over into the receiver, which must be well cooled. The distillate may be freed from excess of oxychloride of phosphorus by re-distillation over acetate of potassium, then distilled by itself, and the liquid which passes over at 55° collected apart. The re-distillation over acetate of potassium is, however, attended with some loss, in consequence of the formation of acetic anhydride.

$$C^2H^3O.Cl + C^2H^3O.K.O = (C^2H^3O)^2O + KCl.$$

For this reason, Ritter recommends the preparation of chloride of acetyl by the action of pentachloride of phosphorus on glacial acetic acid, the product being thereby obtained in larger quantity and more easily purified.

Chloride of acetyl is a colourless, very mobile, strongly refracting liquid, of specific gravity 1·125 at 11°, 1·1305 at 0°, and 1·1072 at 16° (**Kopp**). Boils at 55°. Vapour-density, 2·87 (**Gerhardt**): by calculation (2 vol.) = 2·718. It fumes slightly in the air, and has a pungent odour like that of acetic and hydrochloric acid. The vapour attacks the eyes and respiratory organs very strongly.

Chloride of acetyl is decomposed with explosive violence by water, yielding acetic and hydrochloric acids:

$$C^2H^3OCl + H^2O = C^2H^4O^2 + HCl.$$

Ammonia acts strongly upon it, forming acetamide:

$$C^2H^3O.Cl + H^3N = C^2H^3O.H^2.N + HCl.$$

Similarly with phenylamine, it forms phenylacetamide $C^2H^3O.C^6H^5.H.N$. Distilled with acetate of potassium, it yields acetic anhydride:

$$C^2H^3O.K.O + C^2H^3O.Cl = (C^2H^3O)^2O + KCl;$$

and with benzoate of potassium it forms benzoate of acetyl or acetate of benzoyl:

$$C^7H^5O.K.O + C^2H^3O.Cl = C^2H^3O.C^7H^5O.O + KCl;$$

and similarly with the salts of other acids. With thiacetate of lead, it forms chloride of lead, and probably also thiacetic anhydride:

$$C^2H^3O.Pb.S + C^2H^3O.Cl = (C^2H^3O)^2S + PbCl.$$

When it is heated with zinc in a sealed tube, the metal is strongly attacked; and a black tarry subtance is formed, from which water dissolves chloride of zinc, and separates a liquid having an ethereal odour.

Hydride of Acetyl. See ALDEHYDE.

Iodide of Acetyl. $C^2H^3O.I$.—Obtained by the action of iodide of phosphorus on acetic anhydride (**Guthrie**, Phil. Mag. [4] xiv. 183), or on acetate of potassium; (**Cahours**, Compt. rend. xliv. 1253). After being shaken up with mercury and re-distilled, it forms a transparent colourless liquid, of sp. gr. 1·98 at 17°. It boils at 108° (**Guthrie**); between 104° and 105° (**Cahours**). It fumes strongly in the air, has a very pungent odour, and an intensely sour caustic taste.

Iodide of acetyl is partially decomposed by distillation. Water decomposes it with violence, forming hydriodic and acetic acids. It acts strongly upon alcohol, forming acetate of ethyl. It is decomposed by zinc and by sodium at ordinary temperatures, also by mercury in direct sunshine, iodide of mercury being formed, and little or no permanent gas being given off.

Peroxide of Acetyl. $C^2H^3O.O$. — Discovered by **Brodie** in 1858 (Proceedings of the Royal Society, ix. 361.) It is obtained by mixing acetic anhydride and peroxide of barium, in equivalent proportions, in anhydrous ether. The mixture must be effected very gradually, as it is attended with great evolution of heat. The products are acetate of barium and peroxide of acetyl, the latter remaining dissolved in the ether:

$$(C^2H^3O)^2.O + BaO = C^2H^3O.Ba.O + C^2H^3O.O.$$

The ethereal solution, after filtration from the acetate of barium, is carefully distilled at a low temperature, and the remaining liquid is washed three or four times with water till the wash-water ceases to be acid. The residue is peroxide of acetyl.

It is a viscid liquid, extremely pungent to the taste, the smallest portion placed upon the tongue burning like cayenne pepper. It is a powerful oxidising agent, and highly explosive: a drop heated on a watch-glass explodes with a loud report, shivering the glass to atoms. Baryta-water poured upon it is instantly converted into peroxide of barium, with formation of acetate of barium.

Acetyl-urea. (See UREAS (Compound) and CARBAMIDE.)

ACETYLENE. (See ADDENDA, p. 1111.)

ACETYLOUS ACID. ALDEHYDIC ACID. *Lampic acid, Etheric acid.* An acid supposed to be produced by the slow combustion of ether or of alcohol, and under certain circumstances by the oxidation of aldehyde. When ether is repeatedly distilled, or allowed to fall in successive drops on a solid body heated to about 129°, so that its vapour may come in contact with the air at a high temperature, a disagreeable pungent odour is produced, supposed to be that of aldehydic acid. The compound possessing this odour is formed in larger quantity, when a spiral of fine platinum wire, previously heated to redness, is suspended over a basin containing ether, and the whole covered with a bell-jar. The wire then continues to glow, the ether undergoing a slow combustion without flame, and an acid liquid is formed, which runs down the sides of the bell-jar, and may be collected in a vessel placed below. This liquid is colourless, has a very sour taste, and gives off a pungent vapour which excites tears, and causes great oppression when inhaled. The same compound is obtained, according to Liebig, by heating oxide of silver with aqueous aldehyde; part of the silver is then reduced, while the other portion remains in solution in the form of acetylite of silver, and by decomposing this silver-salt with sulphuretted hydrogen, the acid may be obtained in the free state. It is, however, very liable to decompose, as also are its salts. When the silver-salt is boiled with baryta-water, silver is reduced and acetate of barium remains in solution.

$$\underbrace{2C^2H^3AgO}_{\substack{\text{Aldehydate of}\\\text{silver.}}} + \underbrace{2BaHO}_{\substack{\text{Hydrate of}\\\text{barium.}}} = \underbrace{C^2H^3BaO}_{\substack{\text{Aldehydate}\\\text{of barium.}}} + \underbrace{C^2H^3BaO^2}_{\substack{\text{Acetate of}\\\text{barium.}}} + 2Ag + H^2O$$

Gerhardt (Traité i.) is of opinion that the so-called aldehydic or acetylous acid is merely a mixture of aldehyde and acetic acid, the aldehydate or acetylite of silver being in fact merely aldehyde in which 1 atom hydrogen is replaced by silver.

ACHILLEA MILLEFOLIUM (*Millefoil.*)—The ash of this plant has been analysed by Way and Ogston. 100 parts of the dry herb left 13·45 per cent. ashes containing in 100 parts 30·37 parts of potash, 13·40 lime, 3·01 magnesia, 0·21 sesquioxide of iron, 2·44 sulphuric anhydride, 9·92 silica, 9·36 carbonic anhydride, 7·13 phosphoric anhydride, 20·49 chloride of calcium, and 3·63 chloride of sodium.

ACHILLEIC ACID. An acid said to exist in millefoil (*Achillea Millefolium*). It crystallises in colourless prisms, soluble in 2 parts of water at 12°·5. With the alkalies it forms salts which are easily soluble in water, but sparingly in alcohol. The solutions are precipitated by neutral acetate of lead, whereas the free acid is precipitated by the basic acetate only. The potassium, sodium, and calcium salts are crystallisable: the ammonium and magnesium salts dry up to amorphous masses. The *quinine* salt is said to be obtained in fine crystals grouped in stars, when its aqueous solution is mixed with alcohol, then boiled and left to cool slowly (Zanon, Ann. Ch. Pharm. lviii. 31). Neither the acid nor its salts have been analysed. L. Gmelin, (Handbook, x. 207) suggested that this acid might be impure malic acid. According to Hlasiwetz (J. pr. Chem. lxii. 429) it is aconitic acid.

ACHILLEIN. A bitter substance of unknown composition, extracted by Zanon from millefoil. It forms a hard, yellowish brown extract, having a peculiar odour and bitter taste, easily soluble in water and in boiling alcohol, sparingly in cold alcohol and insoluble in ether; but on treating it with a few drops of any acid, it becomes easily soluble in ether; it dissolves also in ammonia. It is said to be useful as a remedy against fever.

ACHIRITE. (See DIOPTASE.)

ACHMITE. A mineral first distinguished by Ström. It has a brown-black or red-brown colour on the outside, blackish or dark greyish green on the fractured surfaces; in thin fragments it is translucent, and exhibits a yellowish-brown colour. Sp. gr. 3·43 to 3·53. Scratches glass. Melts to a black bead before the blowpipe. It crystallises in oblique four-sided prisms with truncated lateral edges and very sharp four-sided terminal faces, the edges of which correspond with the lateral edges of the oblique prism. It has four cleavages, two parallel to the sides of the oblique prism, and the other two less obvious parallel to the truncations of the acute lateral edges. According to the analyses of Berzelius and Rammelsberg, its composition is $NaO.SiO^3 + Fe^2O^3.\ 2SiO^3$ ($Si = 21{\cdot}5\ .\ 0 = 8$) or $2Na^2O.3SiO^2 + 2(Fe^4O^3,3SiO^2)$ ($Si = 28{\cdot}5\ .\ O = 16$.) It occurs, though rarely, embedded in granite at Eger, and in syenite, near Porsgund in Norway.

ACHROÏTE. A name given to the colourless variety of tourmalin.

ACHTARANDITE. A name given by Breithaupt to a doubtful mineral, hitherto found only in decomposed crystals (trigonal dodecahedrons) which occur in association with vesuvian from Vilui (viluite): they are perhaps derived from helvin.

ACIBROMIDES, ACICHLORIDES, &c. (See OXYBROMIDES, OXYCHLORIDES, &c. &c.)

ACICULITE. (*Acicular Bismuth, Needle ore,*) a native sulphide of bismuth, containing also sulphides of copper and lead. The formula assigned to it by Dana is $(3CuS + BiS^3) + 2(3PbS + BiS^3)$ showing it to be analogous to Bournonite, with which it is isomorphous.

It occurs embedded in white quartz, and accompanying gold, at Beresof, in Siberia.

ACIDIMETRY. The determination of the quantity of real acid in a sample of hydrated acid, is a problem of frequent occurrence, both for scientific and for technical purposes. As the specific gravity of a mixture of acid and water always increases with the proportion of acid present, and as, moreover, a certain specific gravity always corresponds to a certain strength, provided no foreign substances are present, it follows that if the specific gravity corresponding to each particular percentage of real acid has once been accurately determined and tabulated, the strength of any given sample of aqueous acid may always be determined by taking its specific gravity and referring to the tables. (See SULPHURIC, NITRIC, HYDROCHLORIC ACID, &c.) This method is in fact much used, the density being generally taken with the specific gravity bottle for scientific purposes, and with the hydrometer for commercial estimations. This method, however, necessarily supposes that the acid is pure; the presence of any foreign substance, such as nitrate of sodium in nitric acid, cream of tartar and extractive or colouring matter in vinegar, &c. would altogether destroy the accuracy of the result. Moreover, in some acids, the specific gravity varies so little for considerable difference of strength, that a very slight inaccuracy of observation entails a large error in the result. In acetic acid, for example (p. 11), an increase of strength amounting to 1 per cent. produces on the average, an increase of density not exceeding 0·0034. For these reasons it is essential, especially for technological purposes, to adopt some ready and exact method of determining the strength of an acid, independently of its specific gravity.

The strength of an acid may be estimated:

a. By *Volumetric analysis*, that is by ascertaining the measured quantity of a standard alkaline solution required to saturate a given volume of the acid. (See ANALYSIS, VOLUMETRIC.)

b. By *Weight analysis*. This mode of estimation might be conducted in various ways: for instance, by converting a given quantity of the hydrated acid into a neutral salt of potassium, sodium, barium, lead, silver, &c. either by saturation or precipitation, weighing the salt thus formed, and calculating the quantity of acid from its known composition. This method is indeed constantly adopted in scientific chemistry; but is for the most part too tedious for technical purposes. A quicker method is to decompose a known weight of the acid with an excess of acid carbonate of sodium or potassium, and estimate by weight the quantity of carbonic anhydride evolved. The quantity of real acid in the sample of hydrated acid is then easily calculated; for each atom of a monobasic acid, expels 1 atom of carbonic anhydride ($CO^2 = 44$,) and each atom of a dibasic acid expels two atoms of carbonic anhydride ($2CO^2 = 88$): this will be seen from the following equations:

For hydrochloric acid:

$$CO^3NaH + ClH = ClNa + CO^2 + H^2O.$$
$$CO^2 : ClH = 44 : 36{\cdot}5$$

For acetic acid:

$$CO^3NaH + C^2H^3O^2.H = C^2H^3O^2.Na + CO^2 + H^2O$$
$$CO^2 : C^2H^3O^2.H = 44 : 60$$

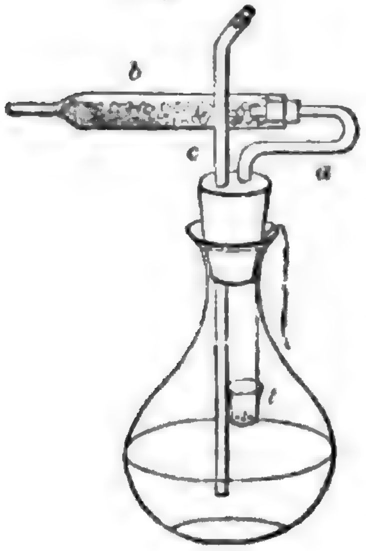
For sulphuric acid:

$$2CO^3NaH + SO^4H^2 = SO^4Na^2 + 2CO^2 + 2H^2O$$
$$2CO^2 : SO^4H^2 = 88 : 98 = 44 : 49$$

Suppose, for example, that 13·5 grm. of hydrated sulphuric acid thus treated with acid carbonate of sodium, eliminate 1·4 grains of carbonic anhydride. The quantity of real acid (SO^4H^2) in the 12·5 grm. is then $1·4 \times \frac{49}{44} = 1·47$ grm. and the quantity of real acid in 100 parts of the hydrated acid will be given by the equation: $x = 1·47 \times \frac{100}{13·5} = 10·89$.

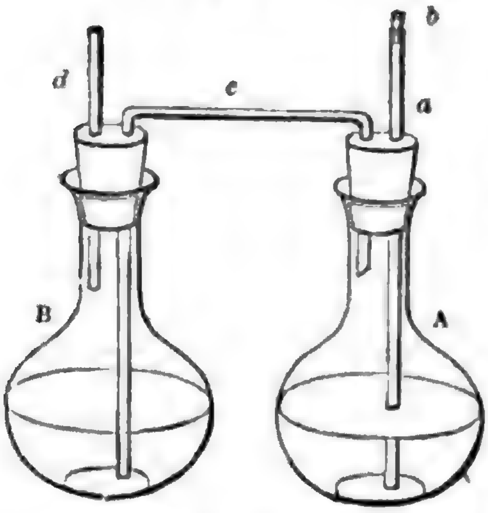
A convenient apparatus for these determinations is a small light glass flask (*fig.* 1) of about100 cubic centimetres (3 or 4 oz.) capacity, having a lipped edge, and fitted with a cork perforated with two holes. Into one of these apertures is fitted a bent tube *a*, carrying a drying tube *b*, filled with chloride of calcium, and into the other, a narrow tube *c*, reaching nearly to the surface of the liquid, and bent at an obtuse angle above the cork. A convenient quantity of the acid whose strength is to be determined, having been weighed out in the flask, a quantity of acid carbonate of sodium or potassium more than sufficient to neutralise the acid, is placed in a small test-tube about an inch long, and having its lip slightly turned over, so that it may be suspended by a thread. This tube is then let down into the flask by the thread, but not low enough to come in contact with the acid; the thread is fixed in its place by inserting the cork into the neck of the flask, and the whole apparatus is weighed. The orifice of the bent tube *c*, is then closed with a plug of cork or wax, the cork of the flask loosened sufficiently to allow the short tube *t*, containing the alkaline carbonate to drop into the acid, and the cork immediately tightened. The carbonate is now decomposed by the acid, and carbonic anhydride escapes through the drying tube, the chloride of calcium retaining any moisture that may be carried along with it. When the effervescence ceases, the flask must be warmed to ensure the complete removal of the carbonic acid from the liquid, and after it has cooled, the plug must be removed from the bent tube *c*, and air drawn through the apparatus by applying the mouth to the extremity of the chloride of calcium tube, in order to remove all the carbonic anhydride remaining in the flask, and replace it by air. The whole is then again weighed, and the loss of weight gives the quantity of carbonic anhydride which has escaped. At the completion of the experiment, a piece of blue litmus paper must be thrown into the liquid in the flask; if it remains blue, the determination may be considered exact; but if it is reddened, there is still free acid in the flask, showing that the quantity of carbonate introduced was not sufficient to decompose it. In that case, a second small tube containing alkaline carbonate must be introduced as before, the apparatus again weighed, and the whole process repeated. The second loss of weight added to the first, gives the total quantity of carbonic anhydride evolved.

Fig. 1.



Another form of apparatus for these estimations, devised by Will and Fresenius, is shown in *fig.* 2. A and B are two small flasks, having strong necks turned over in a lip. Each of them is closed with a tight-fitting cork pierced with two holes. Through the cork of A there passes a straight tube *a*, reaching nearly to the bottom of the flask; a tube *c*, bent twice at right angles, passes through both corks, terminating just below that of A, but reaching nearly to the bottom of the flask B; a straight tube *d* also passes through the cork of B, terminating just below it. The tube *a* is closed at the extremity *b* with a plug of wax. The acid to be estimated is weighed out in the flask A; the other flask B is filled to about one-third with strong sulphuric acid; and the whole apparatus is connected in the manner shown in the figure, the proper quantity of acid carbonate of sodium being introduced into A in a short test-tube, suspended by a thread in the manner described with the former apparatus. The whole apparatus is then weighed, the cork *a* loosened, so as to allow the tube containing the carbonate to fall into the acid, and the cork immediately secured. Carbonic anhydride is now evolved, and is obliged to pass through the sulphuric acid in B, whereby it is completely dried. As soon as gas ceases to escape, the flask A is immersed in water at about 50° or 60° C. till the fresh evolution of gas thereby occasioned ceases. The wax-plug is then loosened, to

Fig. 2.



prevent the sulphuric acid in B from being forced into A, in consequence of diminished pressure in that vessel; the apparatus is removed from the hot water; and air is sucked through the tube *d* as long as any taste of carbonic acid is perceived. Lastly, the apparatus, when quite cold, is re-weighed, and the loss of weight gives the quantity of carbonic anhydride evolved.

This apparatus is much heavier and more bulky than that before described, and does not appear to possess any advantage over it. Mohr points out, as a source of inaccuracy in its use, that the large surface of the two flasks, being heated during the experiment, is not likely, on cooling, to condense exactly the same quantity of moisture as was attached to it before.

It is of the utmost importance that the acid carbonate of sodium or potassium, used in these determinations, be quite pure and free from neutral carbonate. The acid carbonates give a white precipitate with chloride of mercury, and the neutral carbonates a red-brown precipitate; but this test will not indicate the admixture of a small quantity of neutral carbonate with the acid carbonate. A more certain test of purity is to weigh out two equal portions of the acid carbonate, ignite one in a platinum crucible, and determine the quantity of carbonic anhydride given off from the other by the action of the acid in the apparatus represented in *fig.* 2 (See ALKALIMETRY). The quantity of neutral carbonate of sodium remaining after the ignition should be to that of the carbonic anhydride evolved as 53 to 44; and that of the neutral carbonate of potassium to the carbonic anhydride as 69 : 44.

If the acid carbonate is not pure enough to give a white precipitate with chloride of mercury, it should be at once rejected. Commercial acid carbonate of sodium, which will stand that test, may be further purified by triturating it to a uniform powder, covering it with an equal weight of cold distilled water, leaving it for 24 hours, then washing it two or three times on a filter with a small quantity of cold water, leaving it to drain, and drying it by exposure to the air without heating. Acid carbonate of potassium may be purified by recrystallisation. (For further details on Acidimetry, see *Dictionary of Arts, Manufactures, and Mines*, new edition, vol. i. p. 23.)

ACIDS. Salts of hydrogen. The following properties are common to the most important acids,—

1. Solubility in water.
2. A sour taste. (In those acids which possess the most strongly marked characters, this property can be perceived only after dilution with a large quantity of water.)
3. The power of reddening most organic blue and violet colouring matters (for example, litmus), and of restoring the original colour of substances which have been altered by alkalis.
4. The power of decomposing most carbonates, causing effervescence.
5. The power of destroying, more or less completely, the characteristic properties of alkalis, at the same time losing their own distinguishing characters, and forming alkaline salts.

The last is the only one of these properties which can be considered essential to acids; indeed, comparatively few acids possess them all. Moreover, there are many substances which possess, in a greater or less degree, all these properties, but which are never included among acids; of these it will be sufficient to mention *alum* (sulphate of potassium and aluminium). Alum is soluble in water; its solution has a taste which, though not purely sour, approaches much more nearly to sourness than that of many acids (benzoic acid, for example); its solution also reddens litmus, causes brisk effervescence with alkaline carbonates, and neutralises completely the alkalinity of potash or soda, forming an alkaline sulphate.

In order to get a more exact idea of what it is which essentially constitutes acidity, it may be useful to consider briefly the opinions which have successively been held upon the subject by the chemists of past times.

In ordinary language, *acid* is equivalent to *sour;* and in both Greek and Latin, the idea of "sourness" was expressed by almost the same word as that used for "vinegar," the only acid known to the ancients (thus, *Gr.* *ὀξύς*, sour; *ὄξος*, vinegar: *Lat. acidus*, sour; *acetum*, vinegar). It does not, however, appear that very great importance was at any time attached to sourness as a characteristic of acids from a chemical point of view. The number of known acids was first increased by the labours of the Arabian chemists[*]; and the solvent power which many of them exert on substances which are insoluble in water, seems first to have caused them to be regarded as a special class of substances. Thus, **Geber** (middle of the eighth century), who was acquainted

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[*] Almost all the historical statements contained in this article, for which no reference is given, are made on the authority of **Kopp**, "Geschichte der Chemie," 4 vols. 8vo. Brunswick, 1843-47.

with nitric acid and with an impure kind of sulphuric acid, speaks of these bodies under the common name of *aquæ dissolutivæ.* The idea of corrosiveness, or at least a kindred idea, which may perhaps be expressed with tolerable accuracy as that of *chemical activity*, seems to have been long connected by chemists with the idea of acidity. For example, **Van Helmont** (lived 1577 to 1644) attributed the active properties of quick-lime to a peculiar acid, which he supposed limestone to obtain from the fire during burning. **Stahl** (lived 1660 to 1734), who supposed the earths and alkalis to have the same qualitative composition (see Art. ALKALI), represented the alkalis as containing, in larger proportion than the earths, an acid principle to which they owed their greater chemical activity; and even as lately as 1764, a similar idea to that of Van Helmont was applied by **Meyer** to explain a large number of phenomena. This chemist endeavoured to explain the different properties of the caustic and carbonated alkalis and alkaline earths, by supposing the former to be combinations of the latter with a substance which he called *acidum pingue* (fatty acid), because, as he thought, fat-like properties could be perceived by the sense of touch in its combinations with alkalis (caustic alkalis). The idea that corrosiveness is the most important characteristic of acids, was also plainly uppermost in the mind of **Lemery**, when (1675) he attributed the properties of acids to a sharp-pointed form of their smallest particles.

That the properties of acids are, in some important respects, opposed to those of alkalis, was perceived at a comparatively early period. This opposition of properties was in fact the basis of the medical theory of the Iatro-chemists (from the first quarter of the 16th century to the middle of the 17th century). According to them, the constituents of the human body had, some of them an acid, the rest an alkaline nature; the undue preponderance, or want of acidity or of alkalinity was the cause of disease, the condition of perfect health being a particular relation between these two opposing qualities. **Otto Tachenius**, a chemist of this school, gave, in 1668, as the essential character of an acid, its power of combining with alkalis to form salts; and accordingly he included silica among acids. **Boyle** was well acquainted with the properties which are now considered most distinctive of acids. He characterised acids by the solvent power which they exert on various substances with various degrees of energy; by their power of precipitating sulphur and other substances from solution in alkali; by their power of changing the blue colour of many plants to red, and the red of many others to bright red, and of bringing back to their original colour those which have been changed by alkali; and lastly by their forming with alkalis so-called neutral salts, at the same time losing the properties just mentioned. This enumeration of the distinctive qualities of acids differs in no important respect from that given at the beginning of this article.

Various suppositions have been made, from time to time, in order to account for the properties possessed in common by the most strongly marked acids. In order to understand these, it must be borne in mind that the distinction which most chemists are now accustomed to make between acids and salts, dates only from the time of Lavoisier, that is, from the end of the last century; and that, till his time, acids, alkalis, and the substances now by preference called salts, were all included under the common term *salts*. But since the acids then known were comparatively few, and, as was natural, were those of which the acid properties are most evident, the apparent difference between acids and other salts was much greater then than it is now.

The first theory of the constitution of acids was proposed by **Becher** in his "Physica Subterranea," published in 1669. He attributed the common properties of acids to their containing a common principle of acidity (*acidum primigenium*), formed by the union of primitive earth * and water, and supposed that the distinguishing characters of each acid were due to the particular substance which it contained mixed with the primitive acid.

The ideas of **Lemery** regarding acids have already been referred to.

He was followed by **Stahl**, who, in 1723, revived and extended Becher's theory. The following may be taken as a summary of Stahl's views:—The essential properties of all saline substances are: to affect the sense of taste, or to have sapidity; to be soluble in water; and with regard to other chief properties, such as specific gravity and fixity, to be intermediate between water and pure earth. In some salts the saline properties are very marked, in others they are less prominent, and in some they are barely perceptible. Those substances which are most saline, acids and alkalis, have a great tendency to combine with bodies which have not saline properties, and to impart such properties to them. Hence we may conclude that some substances are in themselves essentially saline, while others exhibit saline properties merely because they contain a substance essentially saline as one of their constituents.

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* According to Becher there were three primitive earths,—the vitrifiable, the combustible, and the mercurial,—which were the causes respectively of fusibility, of combustibility, and of volatility; thus corresponding to what the alchemists understood by salt, sulphur, and mercury.

We must regard as belonging to the former class those bodies which not only possess saline properties (taste, solubility, &c.) but which can impart these properties to other bodies by combining with them, and which, when separated from their combinations, recover their original qualities. Hence, all acids and alkalis, fixed and volatile, liquid and solid, must be considered as essentially saline. But, comparing these bodies among themselves, we find that even they possess saline properties in very various degrees. It appears, therefore, that there is only a very small number of actual primitive salts, or rather that there is only one such substance, which is a constituent of all other saline bodies, and is the cause of their saline properties. It is obvious that this substance must be sought among bodies which most distinctly and most invariably manifest saline properties, and which are, at the same time, most simple in their composition. Following this rule, we may at once exclude neutral salts, as being resolvable into more simple saline substances; again, alkalis are more subject to alteration and to loss of their saline properties than acids; they must, therefore, be excluded. Of acids, we may select mineral acids as the most energetic. Lastly, of all mineral acids, *vitriolic* (sulphuric) is the most active, has the greatest solvent powers, adheres most forcibly to the matter dissolved, is the most deliquescent, &c. &c. Accordingly, acids must be considered as the basis of all other saline bodies, and vitriolic acid as the basis of all acids. (Macquer's Dictionnaire de Chimie [1st. Edit. published anonymously, Paris, 1766] Articles "Acide" and "Sel;" Kopp, iii. 15; also Encyclopédie, ou Dictionnaire raisonné des Sciences, des Arts, et des Métiers, * * mis en ordre et publié par MM. Diderot et D'Alembert, t. xiv. [Neufchâtel, 1765] Article "Sel et Sels." The chemical part of this work was by Malouin).

Such were the ideas respecting acids and the cause of acidity, which, with unimportant variations, were held by almost all chemists until the rise of the antiphlogistic system of chemistry. (See COMBUSTION.) But before the downfall of the older system, chemists had begun to have more exact notions than formerly of what were elementary bodies, and to feel the necessity of considering as elements all bodies which they could not decompose. Hence, although Stahl regarded sulphuric acid as a secondary principle, formed by the union of the primitive principles of earth and water, and the other acids as compounds of sulphuric acid with various substances, many of the last upholders of the phlogistic theory regarded most of the inorganic acids as simple substances. For instance, phosphoric and sulphuric acids were supposed to be elements which, when combined with phlogiston, formed phosphorus and sulphur respectively. Sulphurous acid was one of the few inorganic acids which were regarded as compounds; it was supposed to be sulphuric acid combined with less phlogiston than was needed to convert it into sulphur; or, what was the same thing, to be sulphur deprived of part of its phlogiston.

But all previous ideas about acids were gradually superseded by those of Lavoisier. Having found, experimentally, that carbonic, nitric, phosphoric, sulphurous and sulphuric acids, all contained the then newly-discovered substance — oxygen (discovered August 1st, 1774), Lavoisier concluded that oxygen was a constituent of all acids,— that it was the acidifying principle. (Lavoisier, Traité élémentaire de Chimie (1st edit. 1789), i. 69 *et passim;* Kopp, i. 308; also iii. 17.)

He first proposed this theory of acids in 1778; and, although acids were known in which no oxygen could be detected, nearly all chemists continued for about thirty years to consider the assumption, that acidity was in every case due to the presence of oxygen, as a necessary part of the antiphlogistic doctrine. Berthollet, indeed, as early as 1789, pointed out that hydrosulphuric and prussic acids contained no oxygen; but it was not till about 1810, after Davy's and Gay-Lussac and Thénard's researches on muriatic and oxy-muriatic acids (hydrochloric acid and chlorine) that chemists generally began to admit the existence of acids free from oxygen. The conclusions drawn from these experiments were confirmed by Gay-Lussac's discovery of hydriodic acid in 1814, and by his examination of prussic acid in 1815. From this time, most chemists recognised two classes of acids — those containing oxygen (oxygen-acids), and those containing no oxygen (hydrogen acids). Attempts, however, were still made to discover a constituent common to all acids, to which their common properties could be ascribed. Thus, on the one hand, Berzelius continued till 1820 to assert the necessary existence of oxygen in all acids; while, on the other hand, some chemists maintained that all acids contained hydrogen as an essential constituent.

The latter opinion was advocated by Davy. His ideas about acids appear to have been essentially the following:—No one substance ought to be regarded as the acidifying principle; the chemical properties of acids, as well as of other bodies, depend not only on the nature of their constituents, but also on their corpuscular arrangement. The so-called *hydrated* acids are the only true acids, and have a constitution similar to that of their salts. Hydrated chloric acid is a ternary compound of chlorine oxygen, and hydrogen, analogous to chlorate of potassium, which is a ternary compound of chlorine, oxygen, and potassium. The whole of the oxygen may be removed from the acid, and it will remain acid; the whole of the oxygen may be removed from the neutral salt, and it will remain neutral. We have no proof that in either of these bodies the oxygen is divided between the chlorine and the other constituent, or that either of them contains so-called anhydrous chloric acid. Similarly, there is no proof that sulphates or nitrates contain anhydrous sulphuric or nitric acid. Hydrated sulphuric and hydrated nitric acids are the true acids, and are ternary compounds, like the sulphates and nitrates. (Davy, Journal of Science and the Arts, i. 285—288; also Gilbert's Annalen, liv. 377—381; Phil. Trans. 1815, 212, 213; 218, 219; also Kopp.)

In 1816 Dulong proposed the theory, since known as the binary or hydrogen-theory of acids. He endeavoured to show that all acids were similar in constitution to hydrochloric acid; that they were all compounds of hydrogen with a radicle which was in some cases simple (as in hydrochloric and hydriodic acids), in other cases compound (as in hydrocyanic, oxalic, sulphuric, and nitric acids). His view of the constitution of these acids may be expressed by the following formulæ:—

Hydrochloric acid	$H(Cl)$
Hydriodic	$H(I)$
Hydrocyanic	$H(CN)$ or $H(Cy)$
Oxalic	$H(C^2O^4)$
Sulphuric	$H(SO^4)$
Nitric	$H(NO^6)$

Salts, according to this theory, were represented as compounds of an acid-radicle with a metal instead of with hydrogen; thus:—

Hydrochloric acid	$H(Cl)$	Nitric acid	$H(NO^6)$
Chloride of potassium	$K(Cl)$	Nitrate of potassium	$K(NO^6)$

Dulong's theory resembled Davy's in so far as it restricted the term *acid** to substances containing hydrogen (hydrated acids), and assigned an analogous constitution to acids and their salts, but differed from Davy's theory in representing the atoms of every acid as arranged in a specific manner: namely, all the atoms except hydrogen as grouped together to form a compound radicle.

These views did not attract much attention till they were applied by Liebig, in 1837, to explain the constitution of several organic acids, and of the various modifications of phosphoric acid (Ann. Ch. Pharm. xxvi. 170; Ann. Ch. Phys. lxviii. 70.), and although they are explained and discussed in a large proportion of the Manuals of Chemistry published during the fifteen or twenty years following that date, they have never been generally adopted. Until a comparatively recent date, almost all chemists continued to regard oxygen-acids as a class of bodies essentially distinct from hydrogen-acids and from metallic salts. Confining the name of oxygen-acids to the substances now known as ANHYDRIDES, they regarded oxygen-salts as bodies formed by the direct union of acids with metallic oxides, and recognised no essential distinction between actual hydrated acids (acids in the sense of Davy and of Dulong) and mere solutions of the anhydrides in water.

An important extension in the then existing views respecting acids resulted from the discovery announced by Berzelius, in 1826 (Berzel. Jahresb. vi. pp. 184 *et seq.*), that certain metallic sulphides, such as those of arsenic and antimony, were capable of uniting with the alkaline sulphides so as to form well-defined salts perfectly analogous to those formed by the combination of the corresponding metallic oxides with the alkalis. From this time, the existence of three new classes of acids (and corresponding salts) was recognised, namely, acids in which the oxygen of ordinary acids was replaced by sulphur, or by the analogous elements, selenium and tellurium.

We owe the ideas of the nature of acids, now very generally entertained, chiefly to the advance of organic chemisty, which has brought to light a very large number, not only of new acids, but of new substances of all kinds, whose chemical relations cannot be adequately expressed upon the system formerly universally adopted, of regarding all

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* Notwithstanding the more strict use, which was made by both Davy and Dulong, of the word acid, very many chemists still use it to express bodies belonging to two very different classes: *acids* and *anhydrides*. Thus the bodies HCl, HNO^3, H^2SO^4, N^2O^5, SO^3 are all of them frequently called acids, although the first three possess marked resemblances among themselves and equally marked differences from the other two. Again, the bodies H^2SO^4 and SO^3 are often called by the same name, sulphuric acid, although they cannot be obtained in any case by the same process, and although, when caused to act upon one and the same substance, they almost always give rise to products essentially unlike. This confusion between acids and anhydrides dates from the earliest knowledge of the latter class of bodies, and was caused by the fact that the anhydrides which were first discovered immediately produce acids when they come in contact with water. Thus, Lavoisier, by burning phosphorus in oxygen, obtained phosphoric anhydride, but since the solution of this substance in water contained phosphoric acid, he supposed the anhydride to be the acid, and regarded the real phosphoric acid as a combination of phosphoric acid and water. Similarly, sulphuric acid was looked upon as containing "dry sulphuric acid" (sulphuric anhydride) and water; and all other acids, even those of which the anhydrides were unknown, as nitric and hydrochloric acids, were, in like manner, regarded as compounds of a hypothetical anhydride (often called "real acid") with water.

compound bodies as formed by the union of two molecules possessing opposite electro-chemical characters, or of two groups, which, in their turn, have a similar binary constitution. Among the new theories which were the earliest to be thus introduced into the science, was the "Theory of Chemical Types," which represented chemical compounds as combinations of the elementary atoms held together by the attraction exerted by each atom upon all the rest, and capable of exchanging one or several atoms of one element for an equal number of atoms of another, so as to produce new substances, built up after the same plan or *type* as the original compounds, though one or more of their atoms was of a different nature. According to this view, acids and metallic salts were regarded as bodies of the same class: each acid and its corresponding salts were regarded as compounds formed upon the same type, and differing only from the fact of the acid containing hydrogen in the place of the metal contained in the salts. It will be seen that this manner of representing the mutual relation of acids and salts differed but little from that of Davy.

Another result of the progress of organic chemistry which helped to modify the older notions on these subjects, was the acquisition of more consistent ideas than had previously existed of the relative weights of different substances which are chemically comparable with each other. Thus it was discovered that an atom of water contained twice as much hydrogen as an atom of hydrochloric acid, and therefore, that the so-called monobasic acids, or acids containing the same quantity of hydrogen as hydrochloric acid, could not be compounds of water with anhydrous acids, as had been hitherto supposed. The discovery by Gerhardt in 1852 (Ann. Ch. Phys. xxxvii. 285) of the anhydrides corresponding to several monobasic acids, and the fact of their atomic weights being found to be double the atomic weights of the hypothetical anhydrides of the older theory, confirmed the same conclusion.

It is now clear that acids do not form a class apart, distinguished from other substances by something essentially different in their nature; they are, on the contrary, nothing more than a particular class of salts. The definition of acids as *salts of hydrogen*, first clearly enunciated by Gerhardt[*], and repeated at the head of this article, is an accurate statement of the relations which exist between acids and other chemical substances. This definition is, however, obviously insufficient, without a previous answer to the question — what is a salt? For this we must refer to the article SALT. In that article also the properties which acids possess in common with other salts, and which characterise them as belonging to that class, will be most suitably discussed. In the remainder of this article we shall consider the distinguishing properties of acids as such, and the mutual relations of the principal classes into which acids may be divided.

The mode in which acids most frequently react with other substances is by double decomposition, in which they exchange their hydrogen for metals, or for radicles possessing, to a certain extent, metallic functions. The following reactions are all of this kind: namely, their reactions —

1° With metals, —

$$Zn^2 + H^2SO^4 = H^2 + Zn^2SO^4.$$

2° With metallic oxides, sulphides, and salts generally, —

$$\begin{array}{llll}
KHO & + HCl & = H^2O & + KCl \\
KHS & + HCl & = H^2S & + KCl \\
Pb^2O & + 2HCl & = H^2O & + 2PbCl \\
Fe^2S & + H^2SO^4 & = H^2S & + Fe^2SO^4 \\
2NaCl & + H^2SO^4 & = 2HCl & + Na^2SO^4 \\
KNO^3 & + H^2SO^4 & = HNO^3 & + KHSO^4
\end{array}$$

3° With the hydrates of alcohol-radicles, —

$$\underbrace{C^2H^5.H.O}_{\text{Hydrate of ethyl.}} + HCl = H^2O + \underbrace{C^2H^5Cl}_{\text{Chloride of ethyl.}}$$

4° With various metallic compounds, —

$$\underbrace{C^2H^5Zn}_{\text{Zinc-ethyl.}} + HCl = \underbrace{C^2H^5.H}_{\text{Hydride of ethyl.}} + ZnCl.$$

$$\underbrace{KH^2N}_{\text{Potassamine.}} + HCl = H^3N + KCl:$$

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[*] Précis de Chimie organique (Paris, 1844) i. 70; Introduction à l'étude de la Chimie par le Système Unitaire (Paris, 1848), 103. On the similar characters of acids, or hydrogen-salts, and of metallic salts in general, and on the important differences between them and the anhydrides, comp. Laurent, Méthode de Chimie, pp. 48—56, or Cavendish Society's translation, pp. 39 to 45.

With some substances acids unite directly: namely —

1° With ammonia and its analogues, —

$$\begin{aligned} NH^3 + HCl &= NH^4Cl \\ PH^3 + HI &= PH^4I \\ \underbrace{2NC^6H^7}_{\text{Aniline.}} + H^2SO^4 &= \underbrace{(NC^6H^7)^2.H^2SO^4}_{\text{Sulphate of aniline.}}. \end{aligned}$$

2° With some hydrocarbons, —

$$\underbrace{C^2H^4}_{\text{Ethylene.}} + H^2SO^4 = \underbrace{C^2H^6SO^4}_{\text{Sulphovinic acid.}}$$

$$\underbrace{C^3H^6}_{\text{Propylene.}} + HCl = \underbrace{C^3H^7Cl}_{\text{Chloride of trityl.}}$$

Reactions such as the above can be produced by all well characterised acids. The majority of acids can also produce other reactions of various kinds, some of which are characteristic of individual acids, while others are common to a considerable number, and therefore serve for their division into classes. The rational formulæ by which the various acids are commonly represented, indicate the nature of their leading reactions, and hence to the class to which they belong.

Oxygen-acids form by far the most numerous and important class of acids. We may take acetic acid as a special example, and show how the double decompositions which it is capable of undergoing, in common with the other acids of this class, lead to the choice of the rational formulæ by which oxygen-acids in general are usually represented.

1. When acetic acid is converted into an acetate by acting upon it with an oxide, metal, or any other substance, it loses hydrogen. This may be represented by writing one atom of hydrogen in its formula apart from the rest: $C^2H^4O^2 = C^2H^3O^2,H$.

2. By perchloride of phosphorus acetic acid is converted into chloride of acetyl, and loses one atom of oxygen and one atom of hydrogen. To express this, we must write the formula of acetic acid thus; $C^2H^3O.HO$.

3. By the action of pentasulphide of phosphorus, acetic acid loses half its oxygen, and becomes thiacetic acid, $5(C^2H^4O^2) + P^2S^5 = 5(C^2H^4OS) + P^2O^5$.

The rational formula derivable from this reaction is $C^2H^4O.O$.

Combining these three expressions, we come to divide the formula of acetic acid into three parts H, C^2H^3O and O, and to write it $\begin{matrix}C^2H^3O\\H\end{matrix}O$, or $H.C^2H^3O.O$, or in some similar way. This formula indicates beforehand all the most frequent double decompositions of which acetic acid is capable; viz. the separation of one atom of hydrogen, the other atoms remaining together (formation of acetates); the separation of one atom of hydrogen and one atom of oxygen, leaving the group C^2H^3O (formation of chloride of acetyl, of acetamide &c.); the separation of one atom of oxygen, leaving the remaining atoms combined (formation of thiacetic acid, &c.)

The large number of acids which resemble acetic acid as to their leading double decompositions, receive similar rational formulæ; that is to say, rational formulæ consisting of three parts: namely (1) one or more atoms of hydrogen, (2) one or more atoms of oxygen or sulphur, (3) a radicle, nearly always compound and containing oxygen, sulphur or a similar element. Thus, writing the rational formula of acetic acid $\begin{matrix}C^2H^3O\\H\end{matrix}O$, we write that of benzoic acid $\begin{matrix}C^7H^5O\\H\end{matrix}O$, of pyruvic acid $\begin{matrix}C^3H^3O^2\\H\end{matrix}O$, of oxalic acid $\begin{matrix}C^2O^2\\H^2\end{matrix}O^2$, of phosphoric acid $\begin{matrix}PO\\H^3\end{matrix}O^3$, of thiacetic acid $\begin{matrix}C^2H^3O\\H\end{matrix}S$, of sulphocarbonic acid $\begin{matrix}CS\\H^2\end{matrix}S^2$, of sulphocyanic acid $\begin{matrix}CN\\H\end{matrix}S$, of hypochlorous acid $\begin{matrix}Cl\\H\end{matrix}O$.

If in any of these formulæ we replace the radicle by its equivalent quantity of hydrogen (see EQUIVALENTS) and the sulphur (where it occurs) by its equivalent of oxygen, we obtain the formula of one, two, or three, atoms of water $\begin{matrix}H\\H\end{matrix}O$, $\begin{matrix}H^2\\H^2\end{matrix}O^2$, or $\begin{matrix}H^3\\H^3\end{matrix}O^3$. Moreover, the decompositions of which water is susceptible are essentially quite similar to those of acetic acid. Thus, when converted into a hydrate by the action of a metal or of an oxide, water loses one atom of hydrogen—$K + H^2O = H + HKO$, or $Ca^2O + H^2O = CaHO + HCaO$; oxychloride of phosphorus converts water into hydrochloric acid, removing from it one atom of hydrogen and one atom of oxygen.

$3H^2O + POCl^3 = 3HCl + PO^4H^3$; lastly, pentasulphide of phosphorus converts it into hydrosulphuric acid, removing from it one atom of oxygen: — $5H^2O + P^2S^5 = 5H^2S + P^2O^5$. It is in this sense that water is taken as the *type*, or standard of comparison for acetic acid and all other acids which undergo similar double decompositions.

Another class of acids are, in the same way, referred to the type hydrochloric acid, HCl. These acids are susceptible of only one kind of double decomposition: their atoms are separable into only two groups, hydrogen and a radicle. Hydrobromic acid HBr, hydriodic acid HI, hydrocyanic acid HCN, are of this class.

There is still a third class of acids which may be referred to the type ammonia, NH^3. Succinimide, $C^4H^5NO^2$, cyanic acid (carbimide), CONH, and sulphocyanic acid (sulphocarbimide), CSNH, are acids of this kind. Under the influence of metallic oxides, and hydrates they part with one atom of hydrogen, and take up in exchange an atom of metal:

$$\underbrace{2(C^4H^5NO^2)}_{\text{Succinimide.}} + Ag^2O = \underbrace{2(C^4H^4AgNO^2)}_{\text{Argento-succinimide.}} + H^2O.$$

$$\underbrace{CHNO}_{\text{Cyanic acid.}} + HKO = \underbrace{CKNO}_{\text{Cyanate of potassium.}} + H^2O.$$

When boiled with dilute acids, they break up into two groups, a carbonised radicle on the one hand (which combines with oxygen or with oxygen and hydrogen derived from the water of the dilute acid), and the group HN (which combines with two atoms of hydrogen) on the other hand.

$$\underbrace{CHNO}_{\text{Cyanic acid.}} + H^2O = \underbrace{CO.O}_{\text{Carbonic anhydride.}} + \underbrace{HN.H^2}_{\text{Ammonia}}.$$

$$\underbrace{C^4H^5NO^2}_{\text{Succinimide.}} + 2H^2O = \underbrace{C^4H^4O^2.H^2O^2}_{\text{Succinic acid.}} + HN.H^2$$

These reactions show that the rational formulæ of these acids must consist of three parts; an atom of nitrogen, an atom of hydrogen, and a radicle composed of the remaining atoms. Thus the formula of succinimide must be $N.H.C^4H^4O^2$ or $N\left\{\begin{matrix}C^4H^4O^2,\\ H\end{matrix}\right.$ that of cyanic acid N.H.CO, or $N\left\{\begin{matrix}CO\\ H\end{matrix}\right.$. The substance called by Gerhardt nitride of benzoyl, sulphophenyl and hydrogen ($C^{13}H^{11}SO^3N$) is another acid deriving from the type ammonia. Its decompositions have not yet been much studied, but its behaviour with metallic oxides and its formation from ammonia by the successive action of the chlorides of sulphophenyl and of benzoyl ($C^6H^5SO^2Cl$ and C^7H^5OCl) require that its rational formula should be composed of the four parts N, H, $C^6H^5SO^2$ and C^7H^5O. Since the constituent atoms of this acid are separable into four groups, it is evidently susceptible of undergoing even more numerous decompositions than either the acids deriving from the type H^2O, or those previously mentioned as deriving from the type NH^3, whose atoms are separable into only three groups.

In regard to their *chemical constitution*, we may thus divide acids into three principal classes, which have the same mutual relations of formation and decomposition as hydrochloric acid[*], water, and ammonia, and which may therefore be regarded as deriving from these bodies as types.

But, in the same sense as some of the acids which we have been considering, are formed from two, or from three atoms of the same type (from H^2Cl^2, H^4O^2, H^6O^3, &c.), there are certain others which are formed from two or more atoms of two (or perhaps three) different types; for example, sulphuric acid SO^4H^2, derives from the type $\left.\begin{matrix}H^2\\ H^2\end{matrix}\right\}O^2$, thus $\left.\begin{matrix}(SO^2)''\\ H^2\end{matrix}\right\}O^2$, while sulphamic acid, SO^3H^3N, and chlorhydrosulphuric acid, SO^3HCl, derive respectively from the double types $\left.\begin{matrix}H^3N\\ H^2O\end{matrix}\right\}$ and $\left.\begin{matrix}HCl\\ H^2O\end{matrix}\right\}$; thus $\left.\begin{matrix}(SO^2)''\ N\\ H^3O\end{matrix}\right\}$ = sulphamic acid; $\left.\begin{matrix}(SO^2)''\ Cl\\ H\ \ \ \ O\end{matrix}\right\}$ = chlorhydrosulphuric acid. Acids of this kind may be called, for the sake of distinction, *intermediate* acids. The so-called *amic acids* (see AMIC ACIDS) afford the most numerous and best known illustrations of this

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[*] Since the reactions of the acids of the first class are also possessed by those of the second and third classes, it is plain that, if we have regard to these reactions only, all acids may be referred to the type *hydrochloric acid*. To this extent, but no further, the hydrogen-theory represents correctly the constitution of all acids.

class. Like sulphamic acid, they derive from the type $\left.\begin{matrix}H^2N\\H^2O\end{matrix}\right\}$. They can give rise to two kinds of double decomposition; that is, they can decompose either as hydrates (derivatives of water), or as amides (derivatives of ammonia), according to the nature of the body with which they react. In like manner, chlorhydrosulphuric acid and analogous substances can decompose either as hydrates or as chlorides (derivatives of hydrochloric acid).

Another way in which acids may be classified has reference to their *basicity*: they may be divided into *monobasic*, *dibasic*, and *tribasic** acids. Graham was the first to call attention to the existence of polybasic acids in his paper on arsenic and phosphoric acids (Phil. Trans. 1833, 253; Phil. Mag. iii. 451, 469). The distinctions which he established between monobasic and polybasic acids, had reference merely to the composition of their salts. In 1837 Liebig (Ann. Ch. Pharm. xxvi. 138; Ann. Ch. Phys. lxviii. 35) showed that tartaric, citric, meconic, and some other organic acids were polybasic, but he pointed out no new general characters of polybasic acids, nor any new way of distinguishing them from monobasic acids. Gerhardt (Précis de Chimie Organique (1844), i. 71—84) was the first to connect the basicity of acids with other facts than the composition of their metallic salts, and he and Laurent (Ann. Ch. Phys. [3] xviii. 266; Méthode de Chimie, 62—76, or Cavendish Society's Translation pp. 50—62) first placed the question on its present footing.

Mono-, di-, and tri-basic acids may be defined, in a few words, as containing respectively, *one*, *two*, and *three* atoms of hydrogen replaceable by other metals, or by compound groups of analogous function. This definition, taken by itself, is, however, obviously insufficient to decide the basicity of any particular acid, since, by properly multiplying or dividing its formula, we can represent it as possessing whatever basicity we please. Hence, before we can decide what the basicity of an acid is, we must know its atomic weight, and conversely, in order to fix the atomic weight of an acid we require to know its basicity: in other words, the determination of its basicity and the determination of its atomic weight are the same thing.

To decide either of these points, we must take into consideration the general behaviour of the acid with other bodies, and the nature of its derivatives. The following are the most important general differences shown by acids of different degrees of basicity:—

a. Each *monobasic* acid can form *but one* ether. This is neutral in its properties. Two volumes of its vapour contain only *one* volume of ethyl, or alcohol-residue. Monobasic acids do *not* form acid ethers.	*a.* Each *dibasic* acid can form *two* ethers; one of them neutral, the other acid. (Thus, sulphuric acid forms sulphate of ethyl and ethyl-sulphuric acid.) Two volumes of the vapour of the neutral ether contain *two* volumes of ethyl or alcohol-residue.	*a.* Each *tribasic* acid can form *three* ethers; one of them neutral, the other two acid. (*e.g.* phosphoric acid forms phosphate of ethyl and monethyl- and diethyl-phosphoric acids.) Two volumes of the vapour of the neutral ether contain *three* volumes of alcohol-residue.
b. Monobasic acids cannot form stable, well-defined acid salts, or salts with two or more metallic bases.	*b. Dibasic* acids can form, with each metallic base, a neutral salt and an acid salt, which last is exactly intermediate in composition betweeen the neutral salt and the free acid. They can also form well-defined double salts containing two metallic bases, as well as hybrid salts containing two or more metallic bases in indefinite proportions.	*b. Tribasic* acids can form *three* salts with the same metallic base, two of them acid, and one neutral. They can also form double, triple, and hybrid salts.
c. Monobasic acids cannot form double or multiple ethers, that is, ethers containing two or more kinds of alcohol-residue.	*c. Dibasic* acids can form double ethers, that is, ethers containing two kinds of alcohol-residue. (Example, double oxalate of ethyl and methyl.)	*a.*

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* It is probable that tetrabasic acids also exist, but none have yet been much investigated: pyrophosphoric and silicic acids seem to be such.

The above distinctions apply to acids of all kinds, from whatever type they derive. The following apply only to acids which derive from the type *water* (oxacids).

d. Each *monobasic* oxacid can form a chloride, in two volumes of the vapour of which is contained only *one* volume of chlorine. Each such chloride can take up an atom of oxygen and an atom of hydrogen in exchange for an atom of chlorine to re-form the normal acid,—but there is no compound intermediate in composition between the chloride and the normal acid.	*d.* Each *dibasic* oxacid can form a chloride, in two volumes of the vapour of which are contained *two* volumes of chlorine. Dibasic oxacids can also form chlorides which contain, in two volumes of vapour, only *one* volume of chlorine, and are exactly intermediate in composition between the chlorides last-mentioned and the normal acids; that is, they can take up an atom of chlorine in exchange for an atom of oxygen and an atom of hydrogen, to form chlorides containing two volumes of chlorine in two volumes of vapour; or they can take up an atom of oxygen and an atom of hydrogen in exchange for an atom of chlorine, to re-form the normal acid. Thus, sulphuric acid, SO^4H^2, forms chloride of sulphuryl or chlorosulphuric aldehyde SO^2Cl^2, and the intermediate compound chlorhydrosulphuric acid, SO^3HCl.	*d.* Each *tribasic* oxacid can form a chloride in two volumes of the vapour of which are contained *three* volumes of chlorine.
e. Monobasic oxacids, by reacting with ammonia, or its derivatives, form neutral amides, in two volumes of the vapour of which is contained only *one* volume of nitrogen. There are no compounds intermediate between these amides and the corresponding acids.	*e. Dibasic* oxacids, by reacting with ammonia, or its derivatives, form neutral amides, in two volumes of the vapour of which are contained *two* volumes of nitrogen. Intermediate in composition between these amides and the corresponding acids are compounds, generally acid (amic acids), in two volumes of the vapour of which is contained but *one* volume of nitrogen. For, example, oxalic acid, $C^2O^4H^2$, forms neutral oxamide, $C^2O^2H^4N^2$, and the intermediate compound oxamic acid $C^2O^3H^3N$.	*e. Tribasic* oxacids, by reacting with ammonia, or its derivatives, form neutral amides, in two volumes of the vapour of which are contained *three* volumes of nitrogen. Intermediate in composition between each of these amides and the corresponding acid, there may exist two acid compounds, one monobasic and containing in two volumes of vapour *two* volumes of nitrogen: the other dibasic and containing in two volumes of vapour only *one* volume of nitrogen. For example, citric acid, $C^6H^8O^7$, forms with phenylamine (aniline) neutral citrophenylamide, $C^6H^8O^4Ph^3N^3$, ($Ph = C^6H^5 =$ phenyl), and the intermediate monobasic citrodiphenylamic acid, $C^6H^8O^5Ph^2N^2$; the dibasic citromonophenylamic acid, $C^6H^8O^6PhN$, has not yet been discovered.
f. Monobasic oxacids do not form acid compounds (so-called conjugate acids) by reacting with hydro-	*f. Dibasic* oxacids form acid compounds (conjugate acids) by reacting with hydrocarbons or other neu-	*f. Tribasic* oxacids form acid compounds by reacting with hydrocarbons or other neutral substances. For

carbons, or other neutral substances.	tral substances. For example, sulphuric acid reacts with benzene to form sulphobenzidic (phenylsulphurous) acid, and with glycerin to form sulphoglyceric acid.	example, phosphoric acid reacts with glycerin to form phosphoglyceric acid.

(Compare Odling, Chem. Soc. Qu. J. xi. 127.)

In addition to these, other properties of acids might be mentioned, which are connected more or less intimately with their basicity; but, notwithstanding the number of comparatively very well-defined characters which they severally possess, it is impossible to establish any absolute distinction between monobasic and dibasic, or between dibasic and tribasic acids. There are many acids, which, in relation to a particular set of reactions, have the properties of monobasic acids, but, in relation to another set of reactions, behave like dibasic acids; others, again, appear from one point of view to be dibasic, while from another point of view they seem to be tribasic. This will appear more distinctly by considering what degree of generality belongs to each of the differences we have pointed out between acids of different basicities.

a. Number of ethers. Perhaps the only exception to this law is afforded by phosphorous acid, which forms three ethers, one of them containing, in two volumes of vapour, three volumes of alcohol-residue, although, as regards its metallic salts, it is only dibasic.

b. Number of metallic salts. Acetic and formic acids, which possess in a special degree most of the characters of monobasic acids, form, each of them, two potassium- and two sodium-salts.

c. Multiple ethers. No exception to this law is known so far as regards mono- and di-basic acids. Tribasic acids ought by analogy to form ethers containing two or three kinds of alcohol residue; none such have yet been obtained, but there is no reason to suppose that they might not easily be formed.

d. Number of chlorides. Some acids, which according to *a*, *b*, and *c* would be classed as monobasic, form chlorides containing two volumes of chlorine, as well as intermediate chloracids. For instance, Wurtz's *chlorure d'acétyle chloré*, $C^2H^2Cl^2O$ (Ann. Ch. Phys. [3] xlix. 60) reacts with one atom of water to form chloracetic acid, $C^2H^3ClO^2$; and this, with a second atom of water, forms glycollic acid, $C^2H^4O^3$. These three bodies are therefore related in the same way as chloride of sulphuryl, chlorhydrosulphuric acid, and sulphuric acid. Again, lactic acid, $C^3H^6O^3$, a homologue of glycollic acid, is decomposed by pentachloride of phosphorus, giving chloride of lactyl, $C^3H^4Cl^2O$, which reacts with alcohol to form chloropropionate (chlorhydrolactate) of ethyl, $C^5H^9ClO^2$, (Wurtz, Ann. Ch. Pharm. cvii. 192); that is to say, the ether of an acid intermediate between chloride of lactyl and lactic acid. The intermediate acid itself is produced $C^3H^5ClO^2$, by the action of chloride of lactyl on water. (Ulrich, Chem. Soc. Qu. J. xii. 23; Ann. Ch. Pharm. cix. 268.) So far then as their chlorides are concerned, glycollic and lactic acids resemble dibasic and not monobasic acids. (See also observations on *e.*)

In the case of tribasic acids, no intermediate chloracids are known, such as would correspond to chlorhydrosulphuric acid and other derivatives of dibasic acids. It is probable that each tribasic acid can form two such compounds, that phosphoric acid (PH^3O^4), for example, can form chlorhydrophosphoric acid (PH^2ClO^3,) dibasic?) and dichlorhydrophosphoric acid[*] ($PHCl^2O^2$, monobasic?)

e. Number and nature of amides. Some monobasic acids form amides containing, in two volumes of vapour, two volumes of nitrogen. For instance, acetic acid forms *acediamine*, $C^2H^6N^2$, between which and acetic acid $C^2H^4O^2$, acetamide C^2H^5NO is exactly intermediate, (just as oxamic acid, $C^2H^3NO^3$, is intermediate between oxamide, $C^2H^4N^2O^2$, and oxalic acid, $C^2H^2O^4$); acetamide, however, is neutral, not acid, in its properties.

Certain other acids, generally considered monobasic, form amides containing one atom of nitrogen, which possess some of the properties of acids. Thus glycollic acid, $C^2H^4O^3$, forms glycocoll, $C^2H^5NO^2$, a substance capable of acting as an acid, and possessing the same relation of composition to glycollic acid, that oxamic acid does to oxalic acid, or acetamide to acetic acid. The so-called benzamic, toluamic, cuminamic, &c. acids, are substances of a similar constitution: they are to oxybenzoic, oxycuminic, &c. acids what glycocoll is to glycollic acid. In short, glycollic and similar acids, though in the strict sense *monobasic* are *diatomic;* that is, they form but one salt

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[*] Chlorhydrosulphuric acid is formed when sulphuric anhydride is brought in contact with dry hydrochloric acid ($SO^3 + HCl = SHClO^3$). Similarly, a liquid, which probably contains one or both of the compounds mentioned in the text, is formed when phosphoric anhydride is exposed to dry hydrochloric acid ($P^2O^5 + 3HCl = PH^2ClO^3 + PHCl^2O^2$—?)

with each metallic base—are monobasic as regards their metallic salts,—but resemble dibasic acids so far as regards their other derivatives (chlorides and amides).

f. Formation of complex acids. The difference in respect of acidity between compounds formed by the reaction of monobasic and of polybasic acids on neutral substances, is a particular case of a general rule which was first announced by Gerhardt (Précis de Chim. Organ. i. (1844) 102; Compt. rend. Trav. Chim. 1845, 161) in the following form; $B = b' + b - 1$, where B denotes the basicity of the body resulting from the the reaction, b and b' the basicities of the reacting substances (the basicities of alkaline or neutral substances, and of mono-, di-, and tribasic acids being estimated respectively as 0, 1, 2, and 3). Strecker (Ann. Ch. Pharm. lxviii. 47) showed that the rule admitted of a somewhat more extended application in the form $B = b + b' - aq$, where aq denotes the number of atoms of water which separate in the reaction. Piria (Ann. Ch. Pharm. xcvi. 381), observing that, when more than two substances reacted upon each other, the number of atoms of water formed was usually one less than the number of reacting substances, expressed the rule of basicity in the following form, $B = b + b' + b'' + \dots - (n-1)$, ($n$ being the number of reacting substances). In all these expressions, one substance only is regarded as the essential product of the reaction, but, if we take into consideration the basicity of all the products (water, hydrochloric acid, &c. as well as more complex substances) and regard water as a monobasic * acid, we arrive at the following expression—*The sum of the basicities of the products of a reaction is equal to the sum of the basicities of the reacting bodies.*

Examples:—

$$\begin{array}{lccccccc} & HCl & + & KHO & = & KCl & + & H^2O \\ \text{Basicities} & 1 & + & 0 & = & 0 & + & 1 \end{array}$$

$$\begin{array}{lccccccc} & H^2SO^4 & + & KHO & = & KHSO^4 & + & H^2O \\ \text{Basicities} & 2 & + & 0 & = & 1 & + & 1 \end{array}$$

$$\begin{array}{lccccccccccc} & H^2SO^4 & + & KHO & + & KHO & = & K^2SO^4 & + & H^2O & + & H^2O \\ \text{Basicities} & 2 & + & 0 & + & 0 & = & 0 & + & 1 & + & 1 \end{array}$$

$$\begin{array}{lccccccc} & \overbrace{C^2H^4O^2}^{\text{Acetic acid.}} & + & \overbrace{C^2H^6O}^{\text{Alcohol.}} & = & \overbrace{C^4H^8O^2}^{\text{Acetate of ethyl.}} & + & H^2O \\ \text{Basicities} & 1 & + & 0 & = & 0 & + & 1 \end{array}$$

$$\begin{array}{lccccccc} & C^2H^4O^2 & + & NH^3 & = & \overbrace{C^2H^5NO}^{\text{Acetamide.}} & + & H^2O \\ \text{Basicities} & 1 & + & 0 & = & 0 & + & 1 \end{array}$$

$$\begin{array}{lccccccccccccccc} & C^2H^4O^2 & + & HCl & + & HBr & + & \overbrace{C^3H^8O^3}^{\text{Glycerin.}} & = & \overbrace{C^5H^8O^2ClBr}^{\text{Acetochlorhydrobromhydrin.}} & + & H^2O & + & H^2O & + & H^2O \\ \text{Basicities} & 1 & + & 1 & + & 1 & + & 0 & = & 0 & + & 1 & + & 1 & + & 1 \end{array}$$

$$\begin{array}{lccccccccccccccc} & \overbrace{PON^3H^6}^{\text{Phosphamide.}} & + & H^2O & + & H^2O & + & H^2O & = & H^3PO^4 & + & NH^3 & + & NH^3 & + & NH^3 \\ \text{Basicities} & 0 & + & 1 & + & 1 & + & 1 & = & 3 & + & 0 & + & 0 & + & 0 \end{array}$$

The application of the rule of basicity to substances which, like glycollic acid, are monatomic in some relations but diatomic in others, or, like phenylic alcohol (carbolic acid), are intermediate between neutral bodies and acids, often leads, as might be expected, to contradictory results. It must be looked upon, not as a law universally true, but as a rule applicable to the majority of cases, and always dependent on our definitions of acidity and basicity. (Comp. Kekulé, Ann. Ch. Pharm. cvi. 130.)

It has been pointed out by Beketoff (Bullet. de l'Académie de St. Pétersbourg, xii. 369) that this law, in any of the forms yet given to it, gives contradictory results when applied to the three following reactions, which nevertheless are strictly comparable with each other.

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* If water be also considered as a *monacid base*, the *acidity* of bases (or the number of atoms of acid with which they react,—a property correlative with *basicity*,) is usually conformable to the following rule:—*The sum of the acidities of the products of a reaction is equal to the sum of the acidities of the reagents.* The representation of water as a monobasic acid and as a monacid base expresses the fact that it easily takes up 1 atom of an electro-positive, or of an electro-negative radicle in exchange for an atom of hydrogen, or, an electro-positive *and* an electro-negative radicle in exchange for the two atoms of hydrogen. The representation of water as a dibasic acid (or as a diacid base) expresses the possibility of replacing both atoms of hydrogen by the same radicle (formation of anhydrides). This replacement though not unfrequent, certainly takes place less readily than the replacement of 1 atom of hydrogen only, or than the replacement of the two by radicles of different electro-chemical qualities. Either view, however, is evidently entirely relative.

$$1.\ \overbrace{C^7H^6O^2}^{\text{Benzoic acid.}} + \overbrace{C^2H^6O}^{\text{Alcohol.}} = \overbrace{C^9H^{10}O^2}^{\text{Benzoate of ethyl.}} + H^2O$$

$$\text{Basicities}\quad 1 + 0 = 0 + 1$$

$$2.\ \overbrace{C^7H^6O^2}^{\text{Benzoic acid.}} + \overbrace{C^2H^4O^2}^{\text{Acetic acid.}} = \overbrace{C^9H^8O^3}^{\text{Aceto-benzoic anhydride.}} + H^2O$$

$$\text{Basicities}\quad 1 + 1 \quad 0 + 1$$

$$3.\ \overbrace{C^2H^6O}^{\text{Alcohol}} + \overbrace{C^4H^4O}^{\text{Methylic alcohol.}} = \overbrace{C^3H^8O}^{\text{Methyl-ethyl ether.}} + H^2O$$

$$\text{Basicities}\quad 0 + 0 \quad 0 + 1$$

According to the conventions which have been made above, the sum of the basicities of the products of the first reaction is equal to the sum of the basicities of the reagents, but in the second reaction it is less, and in the third it is greater. The obviously artificial character of the law of basicity, which is sufficiently shown by these instances, induced Beketoff to propose to compare the whole quantity of replaceable hydrogen in the reagents with that in the products, instead of merely comparing their basicities, or the number of atoms of hydrogen which are easily replaceable by basylous radicles. If the so-called typical formulæ (see FORMULÆ, RATIONAL) are employed in writing the above reactions, it at once becomes evident that in each case the whole quantity of replaceable hydrogen is two atoms, both in the products and in the reagents; and in all regular double decompositions, the whole number of atoms of replaceable hydrogen remains similarly unaltered (For an account of all that is important in Beketoff's paper, and for an extended criticism of the law of basicity, see Kekulé, Lehrbuch d. organisch. Chemie, pp. 210—219.)

A general classification of acids according to their composition cannot yet be given. There are but few elements which are known to form more than two or three distinct acids; and, although many remarkable relations can be pointed out among the acids formed by different elements, these relations are more important as indications of analogies among the elements, than as serving for the classification of the acids themselves.[*] There is, however, one element — carbon — which, in combination with hydrogen and oxygen, forms a very large number of acids, the best known of which, generally exhibit, when compared together, certain gradations of chemical composition and properties, in accordance with which they can be arranged in a number of *homologous series.* (See HOMOLOGY.) The most important of these series are the following: —

a. Monobasic acids represented by the general formula $C^nH^{2n}O^2$.

Formic	acid	CH^2O^2,	Caproic	acid	$C^6H^{12}O^2$,
Acetic	„	$C^2H^4O^2$,	Œnanthylic	„	$C^7H^{14}O^2$,
Propionic	„	$C^3H^6O^2$,	Caprylic	„	$C^8H^{16}O^2$,
Butyric	„	$C^4H^8O^2$,	Pelargonic	„	$C^9H^{18}O^2$,
Valeric	„	$C^5H^{10}O^2$,	Rutic or capric	„	$C^{10}H^{20}O^2$,

&c.

The acids of this series are found in various vegetable and animal products; several of them occur in combination with glycerin as the chief constituents of most natural solid and liquid fats. The first four have been found in mineral waters (Scheerer, Ann. Ch. Pharm. xcix. 257). They are produced artificially by a great variety of processes, the most important of which are the following:

1°. The oxidation of the alcohols $C^nH^{2n+2}O$

$$\underbrace{C^2H^6O}_{\text{Ethyl-alcohol.}} + O^2 = \underbrace{C^2H^4O^2}_{\text{Acetic acid.}} + H^2O.$$

2°. The decomposition of the so-called nitriles, or cyanides of alcohol-radicles, of the formula $C^nH^{2n-1}N$, by alkaline hydrates.

$$\underbrace{C^3H^5N}_{\text{Acetonitrile or cyanide of ethyl.}} + 2H^2O = \underbrace{C^3H^6O^2}_{\text{Propionic acid.}} + NH^3.$$

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[*] For an able exposition of nearly all that can yet be said on this point, see Odling, Phil. Mag. xvlll. 368; also a lecture on "Acids and Salts," delivered by the same at the Royal Institution, 30th March, 1860, Chemical News, i. 220.

3°. The combination of the potassium- and sodium- compounds of the alcohol-radicles C^nH^{2n+1} with carbonic anydride.

$$\underbrace{C^2H^5Na}_{\text{Sodium-ethyl.}} + CO^2 = \underbrace{C^3H^5NaO^2}_{\text{Propionate of sodium.}}.$$

4°. The oxidation, destructive distillation, fermentation, or putrefactive decomposition of complex organic compounds.

When a fixed-alkaline, or alkaline-earthy salt of one of these acids is subjected to dry distillation, a carbonate and an acetone are generally produced. These products are formed by the decomposition of two atoms of the salt.

The dry distillation of a mixture of the fixed-alkaline, or alkaline-earthy, salts of *two* acids of this series gives rise, in like manner, to a carbonate and to an acetone intermediate in composition between the two acetones corresponding to the acids employed.

When one of the salts is a formate, a similar reaction takes place, but an aldehyde is then produced instead of an acetone.

In some cases the dry distillation of salts of these acids produces (besides acetones) aldehydes, or isomeric compounds (butyral, valeral) and hydrocarbons. (See ALDEHYDES, ACETONES.)

When distilled with excess of alkaline hydrate, they give hydrocarbons of the formula C^nH^{n2+2} (hydrides of alcohol-radicles) and alkaline carbonate.

$$\underbrace{C^2H^3KO^2}_{\text{Acet. potassium.}} + HKO = CK^2O^3 + \underbrace{CH^4}_{\text{Hydride of methyl.}}.$$

With pentachoride of phoshorus they produce chlorides of the formula $C^nH^{2n-1}OCl$; *e.g*:—

$$\underbrace{C^2H^4O^2}_{\text{Acetic acid}} + PCl^5 = \underbrace{C^2H^3OCl}_{\text{Chloride of acetyl.}} + POCl^3 + HCl$$

Their alkaline salts distilled with arsenious anhydride give compounds of arsenic with the alcohol-radicles. (See ARSENIC.)

Subjected to electrolysis, they give carbonates, alcohol-radicles, hydrogen and hydrocarbons of the form C^nH^{2n} and C^nH^{2n+2}.

Under the influence of chlorine (or bromine) they lose one or more atoms of hydrogen, and take up in exchange an equivalent quantity of chlorine, forming chloracids whose general properties usually resemble closely those of the normal acids from which they are formed.

$$\underbrace{C^2H^4O^2}_{\text{Acetic acid.}} + Cl^2 = \underbrace{C^2H^3ClO^2}_{\text{Chloracetic acid.}} + HCl.$$

$$\text{,,} \quad + Br^4 = \underbrace{C^2H^2Br^2O^2}_{\text{Dibrom-acetic acid.}} + 2HBr.$$

$$\text{,,} \quad + Cl^6 = \underbrace{C^2HCl^3O^2}_{\text{Trichlor-acetic acid.}} + 3HCl.$$

b. Acids represented by the formula $C^nH^{2n}O^3$, di-atomic, but usually monobasic. The acids of this series differ from those of series *a* by containing three, instead of two, atoms of oxygen.

Carbonic acid	CH^2O^3,
Glycollic „	$C^2H^4O^3$,
Lactic „	$C^3H^6O^3$,
Butylactic „	$C^4H^8O^3$,
Valerolactic „ (Buttlerow)	$C^5H^{10}O^3$,
Leucic „	$C^6H^{12}O^3$.

These acids are formed

1°. By the reaction of the protochloro- or protobromo- derivatives of the acids of series *a* with hydrates.

$$\underbrace{C^2H^3ClO^2}_{\text{Chloracetic acid.}} + HKO = \underbrace{C^2H^4O^3}_{\text{Glycollic acid.}} + KCl.$$

2°. By the oxidation of the diatomic alcohols, $C^nH^{2n+2}O^2$ (glycols).

$$\underbrace{C^2H^6O^2}_{\text{Glycol.}} + O^2 = \underbrace{C^2H^4O^3}_{\text{Glycollic acid.}} + H^2O.$$

3°. By the oxidation of certain amides of animal origin (glycocol and homologues), especially by nitrous acid.

$$\underbrace{C^2H^5NO^2}_{\text{Glycocol.}} + NHO^2 = \underbrace{C^2H^4O^3}_{\text{Glycollic acid.}} + N^2 + H^2O.$$

4°. By fermentation.

The acids of this series are decomposed by heat into anhydrides and water. (In the case of carbonic acid, this decomposition takes place at the ordinary temperature.)

With pentachloride of phosphorus, they produce diatomic chlorides of the formula $C^nH^{2n-2}OCl^2$; *e.g.*

$$\underbrace{C^3H^6O^3}_{\text{Lactic acid.}} + 2PCl^5 = \underbrace{C^3H^4OCl^2}_{\text{Chloride of lactyl.}} + 2POCl^3 + 2HCl$$

Lactic acid heated with hydriodic acid produces water, iodine and propionic acid (Lautemann):

$$\underbrace{C^3H^6O^3}_{\text{Lactic acid.}} + 2HI = \underbrace{C^3H^6O^2}_{\text{Propionic acid.}} + H^2O + I^2$$

This will probably be found to be a general method of converting acids of series *b* into the corresponding acids of series *a*.

c. Dibasic acids represented by the formula $C^nH^{(2n-2)}O^4$. The acids of this series represent the acids of series *b*, in which 2 at. hydrogen are replaced by an equivalent of oxygen.

Oxalic acid	$C^2H^2O^4$	Pimelic acid	$C^7H^{12}O^4$
Malonic „	$C^3H^4O^4$	Suberic „	$C^8H^{14}O^4$
Succinic „	$C^4H^6O^4$	Anchoic „	$C^9H^{16}O^4$
Lipic „	$C^5H^8O^4$	Sebacic „	$C^{10}H^{18}O^4$.
Adipic „	$C^6H^{10}O^4$		

These acids are, for the most part, products of oxidation. They are solid at ordinary temperatures, and are not volatile without partial or complete decomposition. Some of them are decomposed by heat into carbonic anhydride and a monobasic acid of series *a*.

$$\underbrace{C^3H^4O^4}_{\text{Malonic acid.}} = \underbrace{C^2H^4O^2}_{\text{Acetic acid.}} + CO^2.$$

Several of them also produce acids of series *a*, when fused with excess of alkaline hydrate; the reaction is accompanied by evolution of hydrogen (Gerhardt). Suberic and sebacic acids heated with a great excess of baryta, lose the elements of of 2 at. carbonic anydride and yield the hydrocarbons C^6H^{14} and C^8H^{18}; it is probable that other acids of this series would be decomposed in like manner if similarly treated. (Riche.)

Pentachloride of phosphorus reacts on the acids of this series, producing at first the corresponding anhydrides, which are afterwards converted by excess of the chloride into chlorides of the formula $C^nH^{2n-4}O^2Cl^2$; *e.g.*

$$1°.\quad \underbrace{C^4H^6O^4}_{\text{Succinic acid.}} + PCl^5 = \underbrace{C^4H^4O^3}_{\text{Succinic anhydride.}} + 2HCl + POCl^3.$$

$$2°.\quad \underbrace{C^4H^4O^3}_{\text{Succinic anhydride.}} + PCl^5 = \underbrace{C^4H^4O^2Cl^2}_{\text{Chloride of succinyl.}} + POCl^3$$

There is a certain number of acids which do not enter into any of these three series, but which are related to certain members of them in the same way that the acids belonging to the different series are related to each other. For instance, glyoxylic acid, $C^2H^4O^4$, differs from glycollic acid, $C^2H^4O^3$, in the same way that the latter differs from acetic acid, $C^2H^4O^2$; namely, by containing one more atom of oxygen. And just as bromacetic acid when boiled with oxide of silver produces bromide of silver and glycollic acid —

$$\underbrace{C^2H^3BrO^2}_{\text{Bromacetic acid.}} + HAgO = \underbrace{C^2H^4O^3}_{\text{Glycollic acid.}} + AgBr$$

bromoglycollic acid, when similarly treated, yields bromide of silver and glyoxylic acid (Perkin and Duppa), —

$$\underbrace{C^2H^3BrO^3}_{\text{Bromoglycollic acid.}} + HAgO = \underbrace{C^2H^4O^4}_{\text{Glyoxylic acid.}} + AgBr.$$

Similarly, there is the same difference between glyceric acid, $C^3H^6O^4$, (homologous with glyoxylic acid) and lactic acid, $C^3H^6O^3$, that there is between lactic acid and propionic acid, $C^3H^6O^2$. Again, malic and tartaric acids, $C^4H^6O^5$ and $C^4H^6O^6$, differ from succinic acid by containing respectively one and two atoms more oxygen and they can be converted into succinic acid by heating them with hydriodic acid, in the same way that lactic acid can be converted into propionic acid (Schmidt); moreover, dibromosuccinic acid is decomposed, when boiled with oxide of silver, into bromide of silver and tartaric acid, just as dibromacetic acid is decomposed under similar circumstances into bromide of silver and glyoxylic acid (Perkin and Duppa). The same relation that exists between malic and succinic acids exists also between their homologues, tartronic and malonic acids $C^3H^4O^5$ and $C^3H^4O^4$, but in the case of these acids, the conversion of one into the other has not yet been effected. There is little doubt that these acids — glyoxylic and glyceric, tartronic and malic, and tartaric — represent homologous series running parallel with the three first described, but of which the other terms are as yet unknown.

The relation of all the series of acids, of which we have yet spoken, to each other and to the alcohols homologous with common alcohol, glycol, and glycerine, is shown in the following Table, giving the general formulæ of each series. It will be seen that of the formulæ written one above another, each contains one atom of oxygen more than the formula next above it, and that of the formulæ written in the same horizontal line, each contains two atoms of hydrogen less, and one atom of oxygen more, than the one directly to the left of it. Where known, a special illustration of each general formula is given.

	ALCOHOLS.	ACIDS.		
		Monobasic.		
Monatomic.	$C^nH^{2n+2}O$ Propylic, C^3H^8O.	$C^nH^{2n}O^2$ Propionic, $C^3H^6O^2$ and acids of series *a*.	$C^nH^{2n-2}O^3$ Pyruvic, $C^3H^4O^3$?	$C^nH^{2n-4}O^4$
			Dibasic.	
Diatomic.	$C^nH^{2n+2}O^2$ Propylic glycol, $C^3H^8O^2$.	$C^nH^{2n}O^3$ Lactic, $C^3H^6O^3$ and acids of series *b*.	$C^nH^{2n-2}O^4$ Malonic, $C^3H^4O^4$ Succinic, $C^4H^6O^4$ and acids of series *c*.	$C^nH^{2n-4}O^5$ Mesoxalic, C^3H^2O
				Tribasic.
Triatomic.	$C^nH^{2n+2}O^3$ Glycerin, $C^3H^8O^3$	$C^nH^{2n}O^4$ Glyceric, $C^3H^6O^4$	$C^nH^{2n-2}O^5$ Tartronic, $C^3H^4O^5$ Malic, $C^4H^6O^5$	$C^nH^{2n-6}O^4$
Tetratomic.	$C^nH^{2n+2}O^4$	$C^nH^{2n+}O^5$	$C^nH^{2n-2}O^6$ Tartaric, $C^4H^6O^6$	$C^nH^{2n-4}O^7$ Citric, $C^6H^8O^7$

Another series of acids is represented by the general formula $C^nH^{2n-2}O^2$. They are monobasic like the acids of series *a*, but differ from these by containing 2 atoms less hydrogen combined with the same quantity of carbon and oxygen. None of them have yet been very thoroughly investigated, and the empirical composition even of some of them is still open to discussion. The terms of this series hitherto more or less known are —

Acrylic acid . .	$C^3H^4O^2$	Campholic acid . .	$C^{10}H^{18}O^2$
Crotonic „ . .	$C^4H^6O^2$	Moringic „ . .	$C^{15}H^{28}O^2$
Angelic „ . .	$C^5H^8O^2$	Hypogæic „ . .	$C^{16}H^{30}O^2$
Pyroterebic „ . .	$C^6H^{10}O^2$	Oleic „ . .	$C^{18}H^{34}O^2$
Damaluric „ . .	$C^7H^{12}O^2$	Brassic „ . .	$C^{22}H^{42}O^2$

The following dibasic acids represented by the general formula $C^nH^{2n-4}O^4$, are related — so far at least as composition is concerned — to the last series, in the same manner as the acids of series *c* are related to those of series *a*.

Fumaric acid	$C^4H^4O^4$	Terebic	$C^7H^{10}O^4$
Citraconic Itaconic Mesaconic } acids	$C^5H^6O^4$	Camphoric	$C^{10}H^{16}O^4$

There are still two other series of acids, presenting the same mutual relations as the series *a* and *b*, several terms of which have been very fully studied. They are, —

1. Monobasic acids of the general formula $C^nH^{2n-8}O^2$.

Benzoic acid	$C^7H^6O^2$
Toluylic „	$C^8H^8O^2$
Cuminic „	$C^{10}H^{12}O^2$

2. Diatomic acids of the general formula $C^nH^{2n-8}O^3$.

Oxybenzoic acid	$C^7H^6O^3$
Oxytoluylic „	$C^8H^8O^3$
Phloretic „	$C^9H^{10}O^3$
Oxycuminic „	$C^{10}H^{12}O^3$

The position which a few of the yet remaining organic acids occupy in relation to the series already recognised can be indicated with tolerable certainty; but the greater number are still so imperfectly known that they cannot be included in any classification which is not entirely artificial and empirical. — G. C. F.

ACONITIC ACID. $C^6H^6O^6 = \left.\begin{matrix}(C^6H^3O^3)'''\\ H^3\end{matrix}\right\}O^3$ [or $C^{12}H^6O^{12}$]. *Equisetic acid, Citridic Acid.* (Gm. xii. 408; Gerh. ii. 110; iii. 960; iv. 922.)—An acid found in the roots and leaves of monkshood (*Aconitum Napellus*) and other aconites, and in the herb of *Delphinium Consolida*, collected after flowering. It is also produced by the metamorphosis of citric acid under the influence of heat. It exists in the aconite as aconitate of calcium, which crystallises out on evaporating the juice, and on account of its insolubility may by freed from the colouring matters and other impurities, by washing with water and alcohol. The aconitate of calcium is then dissolved in very dilute nitric acid, and the filtered liquid is precipitated with acetate of lead. The aconitate of lead, after being well washed, is decomposed by hydrosulphuric acid, the sulphide of lead filtered off, and the solution which contains the aconitic acid is evaporated to dryness, and the residue treated with ether, in which the acid dissolves, leaving the impurities.

To obtain it from citric acid, the acid is heated till it ceases to give off inflammable vapours; and the residue dissolved in alcohol is treated with hydrochloric acid, by which aconitic ether is formed, and separates on addition of water, as an oily liquid, which by treatment with potash is converted into aconitate of potassium. This salt is next converted into a lead salt, and the acid is liberated by hydrosulphuric acid as in the preceding process.

On evaporating the ethereal solution, it is left as an amorphous mass, very soluble in water, alcohol, and ether. When heated to 160° it is converted into an oily liquid, which is *itaconic acid*, $C^6H^6O^6 = C^5H^6O^4 + CO^2$. It is distinguished from fumaric acid by being more soluble in water, and from maleic acid by not crystallising.

Aconitic acid is tribasic, and forms three classes of salts, viz. $C^6H^3M^3O^6$; $C^6H^3(M^2H)O^6$; and $C^6H^3(MH^2)O^6$. The aconitates of ammonium, potassium, sodium, magnesium and zinc, dissolve readily in water; the rest are insoluble or sparingly soluble. The soluble aconitates form with solutions of lead and silver, white flocculent precipitates, which do not become crystalline either by ebullition or after prolonged immersion in the liquid, whereas the lead and silver precipitates formed by fumaric and maleic acid are crystalline.

With *ammonium* and *potassium*, aconitic acid forms salts, corresponding to each of the three formulæ above given; with *sodium*, a disodic and a trisodic salt. *Aconitate of calcium*, $C^6H^3Ca^3O^6 + 3H^2O$? occurs in large quantity in extract of aconite. It may also be prepared by dissolving lime in aconitic acid, or by precipitating chloride of calcium with aconitate of sodium. It dissolves in 99 parts of cold water, more readily in boiling water. The solution evaporated at a gentle heat, and without agitation, yields a gelatinous mass which dries up to a gum; but if a few crystals of the salt be introduced into the solution, the whole is deposited in delicate crystals. *Aconitate of manganese*, $C^6H^3Mn^3O^6 + 6H^2O$, is obtained by boiling the acid with carbonate of manganese. Small rose-coloured octahedrons, sparingly soluble in cold water. *Aconitate of lead*, $2C^6H^3Pb^3O^6 + 3H^2O$, is sparingly soluble in boiling water, and gives off 6·29 per cent. water at 140°.—*Aconitate of silver*, $C^6H^3Ag^3O^6$. Nitrate of silver is not precipitated by the free acid, but with the alkaline aconitates it forms a white, amorphous, sparingly soluble precipitate, which is partly reduced to the metallic state by boiling with water.

Aconitate of Ethyl, $C^6H^3(C^2H^5)^3O^6$, is prepared by dissolving aconitic acid in five times its weight of absolute alcohol, and saturating the solution with hydrochloric acid. On addition of water, the ether separates in the form of an oily layer.

It is a colourless liquid, having an aromatic odour, and very bitter taste. Boils at 236°, and has a density of 1·074, at 14°.

Aconitanilic acid or *Phenyl-aconitamic acid.* $C^{12}H^9NO^4 = O\left\{\begin{matrix}N(C^6H^3O^3)'''.C^6H^5.\\ H\end{matrix}\right.$ an amic acid formed on the type $O\left\{\begin{matrix}NH^4\\ H\end{matrix}\right.$, three of the hydrogen-atoms in the ammonium being replaced by the triatomic radicle, aconityl, and the fourth by phenyl. It is obtained by the action of water on the (not yet isolated) compound, $C^{12}H^8NO^3Cl$, produced by treating citranilic (phenyl-citramic) acid with perchloride of phosphorus; probably thus:

$$\underbrace{C^{12}H^{11}NO^5}_{\text{Citranilic acid.}} + 2PCl^5 = C^{12}H^8NO^3Cl + 2POCl^3 + 3HCl;$$

and $$C^{12}H^8NO^3Cl + H^2O = C^{12}H^9NO^4 + HCl.$$

When 1 at. citranilic acid is mixed with 2 at. perchloride of phosphorus, added by small portions, and the action is assisted at intervals by a gentle heat, the whole dissolves, forming a yellow liquid; and on treating this liquid with water, hydrochloric acid is evolved, and aconitanilic acid separates in the form of a soft substance, which, by solution in hot water and cooling, may be obtained in small yellow needles, but cannot be rendered colourless even by repeated crystallisation. The acid dissolves sparingly in water, easily in alcohol, and very easily in aqueous ammonia; and the ammoniacal solution mixed with nitrate of silver, yields rose-coloured flakes of the *silver-salt*, $C^{12}H^8AgNO^4$. (Pebal, Ann. Ch. Pharm. xcviii. 83.)

Aconitodianil or *Diphenyl-aconito-diamide*, $C^{18}H^{14}N^2O^3 = N^2.(C^6H^3O^3.)'''(C^6H^5)^2.H$, is produced (together with aconitanilide), by the action of aconitic acid upon aniline:

$$C^6H^6O^6 + 2C^6H^7N = C^{18}H^{14}N^2O^3 + 3H^2O.$$

also by the action of oxychlorocitric acid upon aniline:

$$C^6H^8O^6Cl^2 + 2C^6H^7N = C^{18}H^{14}N^2O^3 + 3H^2O + 2HCl.$$

It is insoluble in water, very sparingly soluble in cold alcohol. From solution in a large quantity of boiling alcohol, it crystallises on cooling in slender, pale yellow needles. (Pebal.)

Aconitanilide or *Triphenyl-aconito-triamide*, $C^{24}H^{21}N^3O^3 = N^3(C^6H^3O^3)'''(C^6H^5)^3.H^3$, appears to be formed simultaneously with aconitodianil, by the action of aconitic acid or oxychlorocitric acid on aniline:

$$C^6H^6O^6 + 3C^6H^7N = C^{24}H^{21}N^3O^3 + 3H^2O$$

and $$C^6H^8O^6Cl^2 + 3C^6H^7N = C^{24}H^{21}N^3O^3 + 3H^2O + 2HCl.$$

It is an amorphous substance, insoluble in water, but very soluble in cold alcohol, and is thereby easily separated from aconito-dianil. (Pebal.)

The amides of aconitic acid have not yet been obtained.

ACONITINE. $C^{30}H^{47}NO^7$ [or $C^{60}H^{47}NO^{14}$]. (Geiger, Ann. Ch. Pharm. vii. 269; Morson, Pogg. xlii. 175; v. Planta, Ann. Ch. Pharm. lxxiv. 245)—The alkaloid contained in the *Aconitum Napellus*, and probably in all the acrid aconites. It is obtained by exhausting the leaves with alcohol, saturating the extract with milk of lime, separating the lime by sulphuric acid, evaporating the filtered solution of sulphate of acontine at a gentle heat to expel the alcohol, then diluting with water, and treating the solution with carbonate of potassium, which precipitates impure aconitine. The product is purified by redissolving it in alcohol, treating the solution with animal charcoal, reconverting the base into sulphate, again decomposing this salt with hydrate of lime, and treating the precipitate with ether, which dissolves nothing but the aconitine.

Pure aconitine is deposited from solution in dilute alcohol in white pulverulent grains, or sometimes in a compact, vitreous, transparent mass. It is inodorous, but has a persistent, bitter, and acrid taste. It dissolves sparingly in cold water, and in 50 parts of boiling water, forming a strongly alkaline solution. It is very soluble in alcohol, less in ether. At 80° it melts into a vitreous mass, without loss of weight; at 120° it turns brown, and at a higher temperature suffers complete decomposition. It is dissolved without colour by nitric acid. Sulphuric acid colours it first yellow, then violet; tincture of iodine forms with it a kermes-coloured precipitate. It is intensely poisonous, $\frac{1}{50}$ of a grain sufficing to kill a sparrow in a few minutes, and $\frac{1}{10}$ of a grain killing it instantly.

The salts of aconitine do not crystallise readily. They are not deliquescent, but dissolve easily in water and alcohol. The solutions yield a precipitate of aconitine with alkalies. The *hydrochlorate*, $C^{30}H^{47}NO^7.2HCl$, is obtained by passing dry hydrochloric acid gas over dry aconitine. Its solution is not precipitated by chloride of platinum, but yields a white precipitate with chloride of mercury, yellow with chloride of gold, and also with picric acid.

ACONITYL. $C^6H^3O^3$; the triatomic radicle of aconitic acid and its derivatives.

ACRENE. A name given by Laurent to the hydrocarbon, C^3H^4. (See ALLYLENE.)

ACROLEIN. C^3H^4O [or $C^6H^4O^2$]. (Redtenbacher, Ann. Ch. Pharm. xlvii. 114; Geuther and Cartmell, ibid. cxii. 1; Hübner and Geuther, ibid. cxiv. 35; Gm. ix. 365; xii. 550; Gerh. i. iv. 779, 914.)—This body constitutes the acrid principle produced by the destructive distillation of fatty bodies, resulting in fact from the decomposition of glycerin. It is also produced by the action of platinum-black or of a mixture of acid chromate of potassium and sulphuric acid on allyl-alcohol, being indeed the aldehyde of the allyl series. (Cahours and Hofmann.) (See ALLYL.)

Acrolein is best prepared by distilling in a capacious retort a mixture of glycerin and acid sulphate of potassium, or phosphoric anhydride. When phosphoric anhydride is used, the distillate consists entirely of acrolein; but the contents of the retort are very apt to froth over. With acid sulphate of potassium, the distillation is easier, but the acrolein is contaminated with acrylic acid, sulphurous acid, and other products. The distillate is collected in a receiver kept very cold, and provided with a long discharge-tube passing into the chimney in order to carry off the vapours, which are intensely irritating to the eyes. To purify the acrolein, it is digested with oxide of lead, which removes the acid impurities, then rectified in the water-bath, dehydrated over chloride of calcum, and again rectified. As acrolein oxidises very rapidly by contact with the air, all these operations must be conducted with a stream of dry carbonic acid gas passing through the apparatus. (Redtenbacher.)

Hübner and Geuther distil 1 pt. of glycerin with 2 pts. of acid sulphate of potassium, over an open flame, the bottom of the flask being protected by wire-gauze, and a quantity of oxide of lead being placed in the receiver to neutralise the acid products. According to these chemists, the process consists of two stages, the acid sulphate of potassium first dissolving in the glycerin, forming glycerosulphate of potassium, with elimination of water, so that the first portion of the distillate consists chiefly of water, with but little acrolein; but, afterwards, when the liquid becomes more concentrated, the glycerosulphate is decomposed, and acrolein passes over with only a small quantity of water. This latter portion of the distillate is subsequently purified as in Redtenbacher's process.

Acrolein is a colourless, limpid, strongly refracting liquid, lighter than water, and boiling at 52°·4 (Hübner and Geuther). Vapour-density 1·897. Its vapour is so intensely irritating, that a few drops diffused through a room are sufficient to render the atmosphere insupportable. It burns readily with a clear bright flame. It dissolves in about 40 parts of water, and very readily in ether. The solutions are neutral at first, but gradually turn acid by contact with the air.

Acrolein cannot be preserved long, even in closed vessels, as it changes spontaneously into a flocculent substance called by Redtenbacher *disacryl*, and more rarely into a resinous substance, *disacryl-resin*. It sometimes solidifies immediately after being prepared, even in sealed tubes. It undergoes the same transformation under water, which at the same time becomes charged with acrylic, formic and acetic acids. Vapour of acrolein passed through a red-hot tube is decomposed, with formation of water and deposition of charcoal.

Caustic alkalis convert acrolein into resinous products. By *oxidising agents* it is converted into acrylic acid. It reduces oxide of silver with considerable evolution of heat, forming acrylate of silver, which remains dissolved. Nitrate of silver forms with aqueous acrolein a white curdy precipitate (probably C^3H^3AgO) which, however, gradually decomposes, yielding metallic silver and acrylate of silver. On adding a few drops of ammonia, and boiling the liquid, the silver is immediately reduced, but not in the specular form as with aldehyde. *Nitric acid* attacks acrolein strongly, converting it into acrylic acid. *Strong sulphuric acid* blackens it, giving off sulphurous anhydride at the same time. With *chlorine* and *bromine*, it forms heavy oils, together with hydrochloric or hydrobromic acid. *Perchloride of phosphorus* acts violently on acrolein, forming dichloride of allylene $C^3H^4.Cl^2$ (see ALLYLENE), and another oily liquid which appears to be isomeric with it. With *acetic anhydride*, it unites directly, forming the compound $C^3H^4O.C^4H^6O^3$, which is identical in every respect with the compound resulting from the action of acetate of silver on dichloride of allylene (Hübner and Geuther), and may therefore be regarded as diacetate of allylene $(C^3H^4)''.(C^2H^3O)^2.O^2$.

Acrolein-ammonia. $C^{12}H^{20}N^2O^3 = C^{12}H^{18}N^2O^2.H^2O$. Acrolein acts strongly on ammonia, forming a solid compound (first obtained by Redtenbacher):

$$4C^3H^4O + 2NH^3 = C^{12}H^{20}N^2O^3 + H^2O.$$

It is best prepared by gradually adding a saturated solution of ammonia-gas in alcohol to an alcoholic or ethereal solution of acrolein, and precipitating by addition of ether. It is a white or yellowish, amorphous, odourless compound which turns brown at a gentle heat and begins to decompose at 100°, giving off volatile basic products. In the moist state it dissolves readily in cold water and warm alcohol; less in hot water. It dissolves readily in acids, and is precipitated therefrom by alkalis and alkaline carbonates. Hence it appears to be a base. Its solution in hydrochloric acid forms with dichloride of platinum, a light yellow precipitate containing, when dried at 100°, $C^{12}H^{18}N^2O^2.2HCl.2PtCl^2$, or $C^6H^{10}NO.HCl.PtCl^2$. (Hübner and Geuther.)

Acrolein with Acid Sulphite of Sodium.—When acrolein is poured into in aqueous solution of acid sulphite of sodium, its odour is destroyed, and by evaporation over the water-bath, a brown deliquescent syrup is obtained which does not deposit crystals, and from which neither acrolein can be separated by boiling with carbonate of sodium, nor sulphurous acid by boiling with sulphuric acid. (Hübner and Geuther.)

Hydrochlorate of Acrolein, $C^3H^4O.HCl$. Produced by passing dry hydrochloric acid gas into anhydrous acrolein in a vessel surrounded by cold water. The viscid product, washed and dried over oil of vitriol in vacuo, yields hydrochlorate of acrolein as a mass of velvety crystals, which melt at 32° into a thick oil, having the odour of rancid fat. It is insoluble in water, but readily soluble in alcohol and ether, on the evaporation of which it remains as a thick oil. It is resolved by heat into acrolein and hydrochloric acid. It is not apparently altered by boiling with water, or by the action of dilute solutions of the alkalis. Heated with ammonia to 100° in a sealed tube, it yields chloride of ammonium and acrolein-ammonia. Strong hydrochloric acid decomposes it, setting the acrolein free; a similar action is exerted by dilute sulphuric or nitric acid. Hydrochlorate of acrolein in alcoholic solution does not combine with dichloride of platinum, and very slowly reduces a boiling ammoniacal solution of nitrate of silver.

Gaseous *hydriodic acid* passed into acrolein exerts a violent action, attended with a hissing noise like that of red-hot iron plunged into water. The product is a resinous body which is insoluble in alcohol, ether, acids and alkalis, gives off iodine when heated, and yields a small quantity of free iodine to bisulphide of carbon.

METACROLEIN. Hydrochlorate of acrolein heated with hydrate of potassium gives off hydrogen, and yields an oily distillate, which solidifies in magnificent colourless, needle-shaped crystals, consisting of metacrolein, a compound isomeric or more probably polymeric with acrolein. It is lighter than water, has an aromatic odour, and a cooling taste with burning after-taste. It melts at 50°, solidifies at about 45°, or volatilises a little before melting, so that it may be distilled with vapour of water. By heat, it is changed into common acrolein. It is not affected by dilute alkalis, but when heated with mineral acids it is changed more or less into acrolein. In a stream of dry hydrochloric acid gas, it melts and is converted into the hydrochlorate of acrolein above described. Hence it is probable that the compound so named is really a ***hydrochlorate of metacrolein***, perhaps $C^6H^8O^2.2HCl$.

Hydriodate of Metacrolein is produced by passing dry hydriodic acid gas over metacrolein, as a heavy yellow liquid which resembles the hydrochlorate in taste and appearance, and after washing in water, shows a tendency to crystallise at ordinary temperatures. When placed over oil of vitriol, it decomposes, turning brown and giving off iodine.

Hydriodic acid gas acts violently upon acrolein, producing a resinous substance which is insoluble in alcohol, ether, acids and alkalis, and gives up iodine when heated or when digested with bisulphide of carbon. (Geuther and Cartmell.)

ACRYLIC ACID. $C^3H^4O^2 = C^3H^3O.HO$ (or $C^6H^4O^4$). (Gm. ix. 369; Gerh. 783; iv. 914.) *Acroleic acid.* This acid, discovered by Redtenbacher, is produced by the oxidation of acrolein. The best agent to employ is oxide of silver, which, when digested with acrolein, yields a deposit of metallic silver, and a solution of acrylate of silver. This salt is decomposed by hydrosulphuric acid, and the acrylic acid thus set free is purified by rectification. It is necessary carefully to cool the vessel during the decomposition of the silver salt; otherwise, the heat developed is so great that an explosion results. The acid is likewise obtained by the action of chromic acid on oxide of allyl. (Hofmann and Cahours.) (See ALLYL.)

When purified, it is a colourless liquid, of an agreeable, slightly empyreumatic odour. It is miscible with water in all proportions, and its boiling-point is intermediate between that of formic and acetic acids.

It is a monobasic acid, its salts having the formula, $C^3(H^3M)O^2$. They closely resemble the formates and acetates, and are generally very soluble in water.

Acrylate of Sodium. $2C^3(H^3Na)O^2 + 5H^2O$, is obtained by saturating the acid with carbonate of sodium and evaporating. It crystallises in transparent prisms.

Acrylate of Barium. $C^3(H^3Ba)O^2$, is also a soluble salt.

Acrylate of Silver, $C^3(H^3Ag)O^2$, forms white needles, having a silky lustre, and very soluble in water.

Acrylate of Ethyl is obtained, though not in the pure state, by distilling acrylic acid, or its sodium or barium-salt with alcohol and sulphuric acid. (Redtenbacher.)

ACTINOLITE. A variety of Hornblende (*q. v.*)

ADAMANT. See DIAMOND. — **ADAMANTINE SPAR.** See CORUNDUM.

ADAPTER or **ADOPTER.** A piece of tube of more or less conical form, used to elongate the neck of a retort, and to connect it with a receiver.

ADHESION. (See COHESION.)

ADHESIVE SLATE. (See SLATE.)

ADIAPHANOUS SPAR. (See GEHLENITE and SAUSSURITE.)

ADINOLE. A compact impure felspar, better known as *petrosilex*. It differs from jaspar, which it otherwise much resembles, in being fusible before the blowpipe.

ADIPIC ACID. $C^6H^{10}O^4 = O^2 \left\{ \begin{matrix} C^6H^8O^2 \\ H^2 \end{matrix} \right.$, [or $C^{12}H^{10}O^8 = C^{12}H^8O^6.2HO$]. A dibasic acid forming the fifth term of the series $C^nH^{2n-2}O^4$ the lowest term of which is oxalic acid, $C^2H^2O^4$, and the highest at present known, sebacic acid, $C^{10}H^{18}O^4$. It is produced by the action of nitric acid on oleic acid, suet, spermaceti, and other fatty bodies. To prepare it, tallow or suet is boiled in a capacious retort with nitric acid of ordinary strength, which must be frequently renewed, and the distillate poured back till the fatty matter disappears and crystals separate on cooling. The liquid is then evaporated over the water-bath till it solidifies in a crystalline mass on cooling; this mass is washed in a funnel, first with strong nitric acid, then with dilute nitric acid, and lastly with cold water; and the acid is finally purified by crystallisation from boiling water (Malaguti). Other acids of the same series are doubtless formed at the same time; but according to Malaguti, the crystals obtained in the manner just described have all the same appearance, excepting the very last. Wirz (Ann. Ch. Pharm. civ. 257) obtains this acid, together with several other members of the series, by the continued action of nitric acid on the solid fatty acids of cocoa-nut oil. The action is continued for several weeks till the mass solidifies to a crystalline magma. This product is resolved by water into a mixture of several acids of the above series, and a heavy oil; and the acids are separated one from the other by fractional crystallisation from water and alcohol, and lastly by fractional crystallisation of the silver-salts. (See ANCHOIC ACID.)

The acid separates from its aqueous solution in crystalline crusts composed of soft, white, opaque, hemispherical nodules, which appear to be aggregations of smaller crystals. According to Wirz, these crystals dried at 100° contain water of crystallisation, their formula being $2C^6H^{10}O^4 + H^2O$ [anal. 46·2, 46·4 and 47·8 p. c. carbon, 6·6 and 6·8 p. c. hydrogen; calc. 46·4 C and 7·0 H]. At 140° they melt and give off water, leaving the anhydrous acid $C^6H^{10}O^4$ [analysis, 48·2, and 48·3 C; 6·8 and 6·9 H; calc. 49. 3 C and 6·8 H]; which soon afterwards sublimes in long slender needles [the sublimed acid gave by analysis 49·5 C and 6·6 H].

100 parts of water at 18° dissolve 7·73 of the crystallised acid: a hot solution which deposited crystals abundantly on cooling, still retained 8·61 pts. of the acid in 100 pts. at 18° (Wirz). The acid dissolves very readily in hot *alcohol* and *ether*.

The *adipates*, $C^6H^8M^2O^4$, are for the most part soluble in water and crystallisable; insoluble in alcohol. The *ammonium*-salt crystallises in needles (Laurent, Bromeis). The *barium*-salt dried over sulphuric acid, forms opaque warty masses not containing water of crystallisation (Wirz). The *strontium*-salt forms microscopic needles containing $2C^6H^8Sr^2O^4 + 3H^2O$ (Laurent). The *calcium-salt* resembles the barium-salt in appearance, but contains 1 atom of water [$C^6H^8CaO^4 + H^2O$] which is given off between 100° and 200° (Wirz). The *silver-salt*, $C^6H^8Ag^2O^4$, obtained by precipitating the ammonium-salt with a considerable quantity of nitrate of silver, is a white powder.

Adipate of Ethyl, $C^6H^8O^4(C^2H^5)^2$, obtained by saturating the alcoholic solution of the acid with hydrochloric acid gas, is a yellowish oil of sp. gr. 1·001 at 20·5° which boils, with decomposition, at 230°. It has a strong odour of apples and a bitter caustic taste. Chlorine decomposes it, giving off hydrochloric acid and forming a viscous mass. (Malaguti.)

ADIPOCERE. (From *adeps*, fat; and *cera*, wax.) A peculiar white substance, produced by the decomposition of animal matters under the influence of moisture and in situations from which the air is excluded. It was first found by Fourcroy in the *Cimetière des Innocents* at Paris. A number of coffins had been piled one upon another, and remained interred for about 20 years. The bodies were found compressed, as it were, at the bottom of the coffins, and converted into a soft white substance resembling cheese, which bore the imprints of the linen in which they had been wrapped. This matter enclosed the bones, which were broken on the slightest pressure. It was found to consist chiefly of margarate of ammonium together with the margarates of potassium and calcium.

ADULARIA. (See Felspar.)

AEDELFORSITE. (See Edelforsite.)

AECIRIN or **AEGYRIN.** (Handwört. d. Chem. i. 169.) A mineral of the augite family, occurring in the neighbourhood of Brevig in Norway, sometimes in very large and well-defined crystals belonging to the monoclinic system, and having the general character and cleavage of augite. Colour greenish-black to leek-green. Lustre vitreous. The edges exhibit various degrees of translucence, down to complete opacity. Sp. gr. 3·43 to 3·50. Hardness about that of orthoclase. The mineral contains a considerable quantity of iron, partly in the state of protoxide, partly of sesquioxide, besides alumina, lime, magnesia, and soda, sometimes also protoxide of manganese and potash, associated with silica, and sometimes with titanic acid. The formula is not perfectly established, but it is probably of the general form,

$$3(M^2O.SiO^2) + n(M^4O^3.3SiO^2) = 3M^2SiO^3 + nM^4Si^3O^9$$

AERATED WATERS. (See Carbonic Acid and Water.)

AEROLITE. (See Meteorite.)—**AEROSITE.** (See Pyrargyrite.)

AESCHYNITE. (Handwört. d. Chem. i. 192.) A mineral occurring at Miask in the Ural, and consisting, according to Hartwall's analysis, of 56 titanic acid, 20 zirconia, 15 ceric oxide, 3·8 lime, 2·6 ferric oxide, 0·5 stannic oxide (making together 97·9), but according to Hermann's more recent analysis, of 25·90 titanic acid, 33·20 columbic acid, 22·20 ceric oxide, 5·12 cerous oxide, 5·45 ferrous oxide, 6·22 oxide of lanthanum, 1·28 yttria, and 1·20 water (= 100·57). By its crystalline form and properties, as well as by its chemical constitution, it appears to be closely related to Polymignite, Polycrase, Euxenite, &c.

AESCULETIN or **ESCULETIN.** $C^9H^6O^4$, or $C^{18}H^6O^8$. A product of the decomposition of æsculin, discovered in 1853 by Rochleder and Schwartz (Ann. Ch. Pharm. lxxxvii. 186; lxxxviii. 356), and independently by Zwenger (ib. xc. 63). It is obtained; 1. By boiling æsculin with hydrochloric or dilute sulphuric acid. The liquid on cooling deposits a crystalline mass which, when washed with cold water, dissolved in hot alcohol, and treated with acetate of lead, yields a lead-compound of æsculetin from which the latter may be separated by hydrosulphuric acid.—2. A cold saturated solution of æsculin mixed with emulsin (the fermenting principle of sweet almonds) and left in a warm place, deposits after a while, small crystals of æsculetin.

Æsculetin forms shining needles or scales which are bitter, sparingly soluble in cold water and alcohol, more soluble in the same liquids when warm, but nearly insoluble in ether. The aqueous solution is fluorescent like that of æsculin (*q. v.*), but in a much less degree; the fluorescence is however considerably exalted by addition of a small quantity of carbonate of ammonium.

When gradually heated, it gives off 6·64 p.c. water at 100, melts above 270°, and then distils with decomposition. Hydrochloric acid dissolves it without alteration; nitric acid converts it into oxalic acid. It is also decomposed by hot concentrated sulphuric acid. It dissolves in alkalis, forming solutions of a fine gold-yellow colour; its solution in boiling aqueous ammonia deposits on cooling a yellow substance, which decomposes rapidly in contact with the air. Æsculetin imparts a dark green colour to ferric salts. It reduces nitrate of silver at the boiling heat; precipitates red oxide of copper from cupric salts dissolved in potash; and forms with acetate of lead a yellow precipitate containing $C^9H^4Pb^2O^4$.

AESCULIC ACID. Obtained as a white precipitate by boiling *saponin* (a substance contained in the horse-chesnut and in many other plants) with dilute hydrochloric or sulphuric acid, or by boiling saponin with potash-ley and decomposing the resulting æsculetate of potassium with an acid. It is insoluble in water, but soluble in alcohol, and is deposited therefrom in granular crystals on cooling. Nitric acid transforms it into a yellow resinous nitro-compound. It is but a weak acid. The alkaline æsculates are soluble in water, and crystallise from solution in alcohol. The formula of æsculic acid, according to Fremy (Ann. Ch. Phys. [3] lviiii. 101) is $C^{26}H^{16}O^{12}$. Bolley (Ann Ch. Pharm. xc. 211), who calls it *sapogenin*, assigns to it the formula $C^{12}H^{18}O^5$. According to Rochleder and Schwarz (Ann. Ch. Pharm. lxxxviii. 357) it is identical with *chinovatic acid* $C^6H^{10}O^2$.

AESCULIN or **ESCULIN.** $C^{21}H^{24}O^{13}$, or $C^{42}H^{24}O^{26}$. (Gerh. iv. 291, Handwört. d. Chem. i. 196.) A crystalline fluorescent substance obtained from the bark of the horse-chestnut (*Aesculus Hippocastanum*) and of other trees of the genera *Aesculus* and *Pavia*. It was first observed by Frischmann, more closely investigated by Trommsdorff the younger in 1835 (Ann. Ch. Pharm. xiv. 198), afterwards by Rochleder and Schwarz (ibid. lxxxvii. 186; lxxxviii. 156), and by Zwenger (ibid. xc. 63).

The aqueous extract of the bark is precipitated with acetate of lead; the precipitate is washed, suspended in water, and decomposed by hydrosulphuric acid; and the liquid is filtered at the boiling heat. Or better: the aqueous extract is mixed with solution of alum and excess of ammonia; the liquid filtered to separate the fawn-coloured precipitate of alumina mixed with the colouring matter of the bark; the yellowish filtrate neutralised with acetic acid and evaporated to dryness; the residue containing the sulphates and acetates of potassium and ammonium, boiled with a little strong alcohol to extract the æsculin; the alcoholic filtrate evaporated till it crystallises; and the æsculin thus obtained, is purified by pressure between bibulous paper, and recrystallisation. (Rochleder, J. pr. Chem. lxxi. 414; Chem. Gaz. 1858, 96.)

Aesculin forms colourless, needle-shaped crystals. It is inodorous, has a bitter taste, is sparingly soluble in cold water and alcohol, more soluble in the same liquids at the boiling heat, and nearly insoluble in ether.

Aesculin is coloured red by chlorine; it forms a yellow precipitate with subacetate of lead, and reduces the protoxide of copper to suboxide, like glucose. It melts at 160° and decomposes at a somewhat higher temperature, yielding various products among which is a small quantity of æsculetine. Boiled with hydrochloric or dilute sulphuric acid, it is resolved into æsculetin and glucose:

$$C^{21}H^{24}O^{13} + 3H^2O = C^9H^6O^4 + 2C^6H^{12}O^6$$

The aqueous solution of æsculin is highly fluorescent (see Light), the reflected light being of a sky-blue colour. Nearly the same fluorescent tint is exhibited by an infusion of horse-chestnut bark. The colour is however slightly modified by the presence of another fluorescent substance, *paviin*, recently discovered by Prof. Stokes (Chem. Soc. Qu. J. xi. 17). The latter is separated from æsculin by its greater solubility in ether. Its solution exhibits a blue-green fluorescence. Aesculin and paviin appear to exist together in the barks of all species of the genera *Asculus* and *Pavia*, æsculin being however more abundant in the former and paviin in the latter (see Paviin). The fluorescence of both æsculin and paviin is augmented by alkalis, but destroyed by acids.

AETHAL. (See Cetyl.)

AETHER, AETHYL, &c. (See Ether, Ethyl, &c.)

AETHIOPS. An old pharmaceutical term applied to various mineral preparations of black colour or approaching thereto: *e. g. Aethiops antimonialis* obtained by triturating together mercury, sulphide of antimony, and sulphur; *Aethiops martialis* black oxide of iron; *Aethiops mineralis*, black sulphide of mercury obtained by triturating mercury with sulphur; *Aethiops narcoticus* (or *hypnoticus*,) sulphide of mercury obtained by precipitation; *Aethiops per se*, the grey powder obtained by exposing impure mercury to the air.

AETHOKIRRIN. The yellow colouring matter of the flowers of *Antirrhinum Linaria*.

AFFINITY. (See Chemical Affinity.)

AFTONITE. (See Aphtonite.)

AGALMATOLITE [from ἄγαλμα, an image; and λίθος, stone]; *Bildstein*. This name was originally given to a soft mineral or rather a number of such minerals used by the Chinese for carving grotesque figures and idols. These minerals vary in colour from greyish-green to yellow and red; they are all more or less soft and unctuous to the touch and capable of being cut and polished.

The Chinese agalmatolites are of three kinds: viz.

1. Hydrated silicates of aluminium and potassium:

a. $9SiO^2.3Al^4O^3.1K^2O.3H^2O = 6SiO^3.3Al^2O^3.1KO.3HO$

b. $3SiO^2.1Al^4O^3.M^2O.1H^2O = 6SiO^3.3Al^2.3MO^{*}.3HO$

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* M denotes potassium, sodium, calcium, magnesium, &c.

2. Hydrated silicates of aluminium.

$$a.\ 9\mathrm{SiO^2.2Al^4O^3.6H^2O} = 3SiO^3.1Al^2O^3.3HO$$
$$b.\ 15\mathrm{SiO^2.4Al^4O^3.4H^2O} = 5SiO^3.2Al^2O^3.2HO$$

3. Hydrated silicates of magnesium:

$$15\mathrm{SiO^2.12Mg^2O.4H^2O} = 5SiO^3.6MgO.2HO$$

There are also several European minerals which in composition and physical character closely resemble the Chinese agalmatolites.

4. Agalmatolite from Magyag in Hungary has the same composition as the Chinese mineral, 1, *a*.

5. Agalmatolite, from Ochsenkopf in the Saxon Harz, and *Onkosin* from Posseggen in Salzburg, have a composition expressed by the formula:

$$9\mathrm{SiO^2.3Al^4O^3.2M^2O.3H^2O} = 6SiO^3.3Al^2O^3.2MO.3HO.$$

6. *Mother of Diaspore*, a mineral in which the diaspore of Schemnitz in Hungary is intergrown, has the composition 2, *a* above.

7. *Parophite* from Canada has a composition corresponding to the formula:

$$9\mathrm{SiO^2.3Al^4O^3.3M^2O.4\tfrac{1}{2}H^2O} = 6SiO^3.3Al^2O^3.MO.4\tfrac{1}{2}HO$$

8. *Dysyntribite*, from Diana and other localities in St. Lawrence county, New York, appears also to have a constitution resembling that of the agalmatolites.

9. *Kaolin*, which is a hydrated silicate of aluminium, containing

$$(2\mathrm{SiO^2.Al^4O^3.2H^2O}) = 4SiO^3.3Al^2O^3.6HO,$$

exactly resembles the agalmatolites in physical character.

10. *Neolite*, from Eisenach and other localities, containing

$$9\mathrm{SiO^2.Al^4O^3.3M^2O.H^2O} = 6SiO^3.1Al^2O^3.3MO.1HO,$$

also forms masses resembling agalmatolite.

All these minerals have a specific gravity ranging from 2·75 to 2·85; rarely as high as 2·90. In hardness, they are intermediate between gypsum and calcspar. They are more or less translucent, unctuous to the touch, do not adhere to the tongue, and are easily carved and wrought.

The true agalmatolites are 1, *a*; 4, 5, 6, and 7: the rest may be regarded as allied species. (Handw. d. Chem. i. 375.)

AGAPHITE. (See TURQUOISE.)

AGAR-AGAR, or Bengal Isinglass: a dried sea-weed from Singapore, consisting of small transparent colourless strips, is almost completely soluble in water, and forms a large quantity of thick, tasteless, and odourless jelly.

AGARICIN. (See AMANITIN.)

AGARICUS. A genus of the order *Fungi*. Many fungi, especially of the genus *Agaricus* are commonly used as food, and it is remarkable that the amount of nitrogen contained in their dried substance exceeds that in peas and beans, which are generally regarded as the most nutritious of all articles of food.

The following table exhibits the percentage of nitrogen and of ash in various species of fungi, as determined by Schlossberger and Döpping (Ann. Ch. Pharm. lii. 106 to 120). The plants were dried at 100° C. The quantity of water averaged about 90 per cent.

	Nitrogen.	Ash.
Agaricus deliciosus	4·68	6·9
„ *arvensis*	7·26	19·82
„ *glutinosus*	4·61	4·8
„ *russula*	4·25	9·5
„ *cantharellus*	3·22	11·2
„ *muscarius*	6·34	9·0
Boletus aurens	4·7	6·80
Lycoperdon echinatum	6·16	5·2
Polyporus fomentarius	4·46	3·0
Dædalea quercina	3·19	3·1

The ash contains a large proportion of phosphates. The solid tissue of fungi, formerly regarded as a peculiar substance, *fungin*, is nothing but cellulose: it may be extracted by treating the fungi successively with water, weak soda-ley, hydrochloric acid, and alcohol. Agarics were found by Schlossberger and Döpping to contain mannite and fermentable sugar, but no starch. The acid contained in agarics and other fungi was formerly supposed to be of peculiar nature, and called *boletic* or *fungic* acid; but it has been shown by Bolley and Dessaignes that many agarics contain fumaric acid, sometimes associated with malic, citric, and phosphoric acid.

AGARICUS MINERALIS, the *mountain milk*, or *mountain meal*, of the Germans, is one of the purest of the native carbonates of lime, found chiefly in the clefts of rocks, and at the bottom of some lakes, in a loose or semi-indurated form.

The name of *mineral agaric*, or *fossil meal*, was also applied by Fabroni to a stone of a loose consistence found in Tuscany in considerable abundance, of which bricks may be made, either with or without the addition of a twentieth part of clay, so light as to float in water, and which he supposes the ancients used for making their floating bricks, This, however, is very different from the preceding, not being even of the calcareous genus, since it appears, on analysis, to be a hydrated silicate of magnesium mixed with lime, alumina, and a small quantity of iron. Kirwan calls it *argillo-murite*.

AGATE. A mineral, whose basis is calcedony, blended with variable proportions of jasper, amethyst, quartz, opal, heliotrope, and carnelian. *Ribbon agate* consists of alternate and parallel layers of calcedony with jasper, or quartz, or amethyst. The most beautiful comes from Siberia and Saxony. It occurs in porphyry and gneiss.—*Brecciated agate;* a base of amethyst, containing fragments of ribbon agate, constitutes this beautiful variety; it is of Saxon origin.—*Fortification agate*, is found in nodules of various imitative shapes, imbedded in amygdaloid. This occurs at Oberstein on the Rhine, and in Scotland. On cutting it across and polishing it, the interior zig-zag parallel lines bear a considerable resemblance to the plan of a modern fortification. In the very centre, quartz and amethyst are seen in a splintery mass, surrounded by the jasper and calcedony.—*Mocha stone.* Translucent calcedony, containing dark outlines of arborisation, like vegetable filaments, is called Mocha stone, from the place, in Arabia, where it is chiefly found. These curious appearances were ascribed to deposits of iron or manganese, but more lately they have been thought to arise from mineralised plants of the cryptogamous class.—*Moss agate*, is a calcedony with variously coloured ramifications of a vegetable form, occasionally traversed with irregular veins of red jasper. Dr. M'Culloch has detected, what Daubenton merely conjectured, in mocha and moss agates, aquatic confervæ, unaltered both in colour and form, and also coated with iron oxide. Mosses and lichens have also been observed, along with chlorite, in vegetations. An onyx agate set in a ring, belonging to the Earl of Powis, contains the chrysalis of a moth.

Agate is found in most countries, chiefly in trap rocks and serpentine. Hollow nodules of agate, called *geodes*, present interiorly crystals of quartz, colourless or amethystine, having occasionally scattered crystals of stilbite, chabasite, and capillary mesotype. These geodes are very common. Bitumen has been found by M. Patrin in the inside of some of them, among the hills of Dauria, on the right bank of the Chilca. The small geodes of volcanic districts occasionally contain water in their cavities. These are chiefly found in insulated blocks of a lava having an earthy fracture. When they are cracked, the liquid escapes by evaporation; it is easily restored by plunging them for a little in hot water. Agates are artificially coloured by immersion in metallic solutions. Agates were more in demand formerly than at present. They were cut into cups and plates for boxes; and also into cutlass and sabre handles. They are still cut and polished on a considerable scale and at a moderate price, at Oberstein. The surface to be polished is first coarsely ground by large millstones of a hard reddish sandstone, moved by water. The polish is afterwards given on a wheel of soft wood, moistened and imbued with a fine powder of a hard red *tripoli* found in the neighbourhood. M. Faujas thinks that this *tripoli* is produced by the decomposition of the porphyrated rock which serves as a gangue to the agates. The ancients employed agates for making cameos (see CALCEDONY). Agate mortars are valued by analytical chemists, for reducing hard minerals to an impalpable powder.

The oriental agate is almost transparent, and of a vitreous appearance. The occidental is of various colours, and often veined with quartz or jasper. It is mostly found in small pieces covered with a crust, and often running in veins through rocks like flint and petrosilex, from which it does not seem to differ greatly. Agates are most prized when the internal figure nearly resembles some animal or plant.—U.

AGEDOÏL. A name applied by Caventou to a crystallisable substance obtained from liquorice-root; identical with asparagin. (Henry and Plisson.)

AGNESITE. Syn. with BISMUTITE.

AGROSTEMMINE. A crystalline basic substance obtained from the seeds of the corn-cockle (*Agrostemma Githago*). The seeds are exhausted with weak alcohol acidulated with acid; the acid is concentrated by evaporation and mixed with magnesia; and the dried precipitate is treated with alcohol.

Agrostemmin crystallises in pale yellow scales which are but slightly soluble in water, but very soluble in alcohol, to which they impart an alkaline reaction. It is decomposed by boiling potash, with evolution of ammonia.

The sulphate, chloro-aurate and chloroplatinate of agrostemmine are crystallisable; the phosphate forms a bulky precipitate. (Schulze, Ann. Ch. Pharm. lxviii. 350.)

AIKINITE. Syn. with ACICULITE.

AIR. The term "air" (Latin, *aer*) is now exclusively employed to denote the component gases of the earth's atmosphere. Amongst the older writers on science, we find the word "air" made use of to designate the gaseous or aeriform condition of a body; thus carbonic acid gas was called "fixed air," hydrochloric acid gas "marine acid air," hydrogen gas "inflammable air," &c. (See ATMOSPHERE.)

AJUGA REPTANS (*Creeping Bugle*). (Handw. d. Chem. i. 385.) This plant, grown on the even ground of the Lechthal, yielded, when gathered in the beginning of June, 84·3 p.c. water, and 10·4 p.c. ash (*a*); that which grew on the chain of hills adjoining the valley, yielded at the end of June, 81·6 p.c. water and 9·5 p.c. ash (*b*).

	a.	*b.*
Potash	37·31	36·39
Soda	—	4·81
Lime	23·73	15·70
Magnesia	10·70	5·43
Sesquioxide of iron	2·79	1·70
Manganoso-manganic oxide	trace	2·29
Phosphoric anhydride	5·46	5·51
Sulphuric	3·63	3·68
Chloride of potassium	5·04	—
Chloride of sodium	2·66	2·78
Silica	8·61	21·71

AKANTICON. (See EPIDOTE.)

AKCETHIN. (See ACETONE.)

AKMITE. (See ACHMITE.)

AKONTITE. A variety of arsenical pyrites.

ALABANDIN. (See MANGANESE-GLANCE.)

ALABASTER. *Granular gypsum, Albâtre gypseux.* The technical name for granular gypsum or sulphate of calcium. Alabaster is among the several varieties of gypsum what marble is among carbonates of calcium, and like marble is used for sculpture, especially for objects of small dimensions. The hard, fine-grained, snow-white, translucent alabaster from Volterra near Florence, is especially valued for these purposes.

ALALITE. (See DIOPSIDE.)

ALANINE. $C^3H^7NO^2$. (A. Strecker, Ann. Ch. Pharm. lxxv. 29; Gm. ix. 434; Gerh. i. 678.) An organic base obtained by heating aldehyde-ammonia with hydrocyanic acid in presence of excess of hydrochloric acid.

$$C^2H^3O^2.NH^4 + CNH + HCl + H^2O = C^3H^7NO^2 + NH^4Cl.$$

To prepare it, an aqueous solution of 2 pts. aldehyde-ammonia is mixed with aqueous hydrocyanic acid containing 1 pt. of the anhydrous acid, hydrochloric acid is added in excess, and the mixture is boiled and afterwards evaporated to dryness over the water-bath. The residue consisting of hydrochlorate of alanine and a large quantity of sal-ammoniac, is digested in a little cold water, which leaves the greater part of the sal-ammoniac undissolved; the solution of hydrochlorate of alanine is boiled with hydrate of lead, added in small portions as long as ammonia continues to escape; the liquid is filtered; and the dissolved lead is precipitated from the solution by sulphuretted hydrogen. The filtered liquid yields crystals of alanine by evaporation, and an additional quantity may be obtained from the mother-liquor by addition of alcohol. Another and better method is to treat the mixture of hydrochlorate of alanine and sal-ammoniac with alcohol and ether, in which the former only is readily soluble, concentrate the solution by evaporation, and remove the hydrochloric acid by boiling with hydrate of lead.

Properties. — Alanine crystallises on cooling from a hot saturated solution in colourless needles having the form of oblique rhombic prisms united in tufts. They have a pearly lustre, are hard, and grate between the teeth. At 200°, it sublimes and falls down again in fine snowy crystals; when rapidly heated, it melts and suffers partial decomposition. It dissolves in 4·6 pts. of water at 17°, and in a smaller quantity of hot water; it is very sparingly soluble in cold alcohol, and quite insoluble in ether. The aqueous solution has a sweet taste, does not affect vegetable colours, and forms no precipitates with any of the ordinary reagents.

Alanine is isomeric with urethane, lactamide, and sarcosine; from the two former it is distinguished by not melting below 100°; from the last by being soluble in water, and by its behaviour with metallic oxides.

Decompositions.—Alanine is not altered by boiling with dilute acids, or with alkalis. It dissolves in strong sulphuric acid, and the solution does not blacken on boiling. Fused with hydrate of potassium, it gives off hydrogen and ammonia, and yields cyanide and acetate of potassium. When its aqueous solution is boiled with peroxide of lead, it is resolved into aldehyde, carbonic anhydride, and ammonia:

$$C^3H^7NO^2 + O = C^2H^4O + CO^2 + NH^3.$$

The aqueous solution is also decomposed by nitrous acid, with evolution of nitrogen and formation of lactic acid:

$$\underbrace{C^3H^7NO^2}_{\text{Alanine.}} + \underbrace{NO^2H}_{\text{Nitrous acid.}} = \underbrace{C^3H^6O^3}_{\text{Lactic acid.}} + 2N + H^2O.$$

Compounds of Alanine.—Alanine acts both as a base and as an acid. It unites directly with acids, and when boiled with metallic oxides forms compounds consisting of alanine with 1 atom of hydrogen replaced by a metal. With *hydrochloric acid*, it forms two compounds, viz. $2C^3H^7NO^2.HCl$, obtained by treating alanine with dry hydrochloric acid gas, and $C^3H^7NO^2.HCl$, produced by evaporating a solution of alanine in excess of hydrochloric acid. Both these compounds dissolve readily in water, sparingly in alcohol; the latter is very deliquescent, but may with some difficulty be obtained in crystals. On mixing a solution of alanine in hydrochloric acid with excess of bichloride of platinum, and evaporating, the chloroplatinate, $2C^3H^7NO^2.HCl.PtCl^2$, crystallises in slender yellow needles, soluble in water and alcohol, and even in a mixture of alcohol and ether. *Nitrate of alanine*, $C^3H^7NO^2,HNO^3$ is obtained by evaporating a solution of alanine in dilute nitric acid, in long colourless needles, which deliquesce in damp air, and dissolve very readily in water, less in alcohol; at 100°, they turn yellow and decompose. *Sulphate of alanine* is very soluble in water, and remains as a syrupy mass when its solution is evaporated; it may be washed with cold alcohol. It is not precipitated from its aqueous solution by alcohol, but a mixture of ether and alcohol separates it in the form of a thick syrup.

The *copper-compound* of alanine, $2C^3H^6CuNO^2 + H^2O$ crystallises from a solution of alanine which has been boiled with cupric oxide, in dark blue needles and thicker rhombic prisms. It forms a dark blue solution in water, but is nearly insoluble in alcohol. The crystals remain unaltered at 100°, but at 120° they give off water, and are reduced to $C^3H^6CuNO^2$ assuming at first a lighter blue colour, and afterwards crumbling to a bluish-white powder. *The silver-compound*, $C^3H^6AgNO^2$, is obtained in a similar manner, and separates as the liquid cools, in small yellow needles united in hemispherical groups. They assume a darker colour when exposed to light, and also when heated to 100° in the moist state; but when dry they sustain that temperature without alteration. A solution of nitrate of silver mixed with alanine, yields by spontaneous evaporation, colourless rhombic tables, which are decomposed by heat, with slight detonation, and leave a residue of spongy silver. A *lead-compound*, $C^3H^6PbNO^2.PbHO$, is obtained in colourless glassy needles, by boiling protoxide of lead in aqueous alanine, and evaporating and cooling the solution. It is also precipitated in radiating crystals, on mixing the aqueous solution with alcohol. The crystals dried over sulphuric acid, give off water and crumble to a powder which is no longer completely soluble in water.

ALANTIN. (See Inulin.)

ALBAN. A white, crystalline, resinous substance extracted from gutta percha by alcohol or ether. It is best obtained by treating gutta percha with ether, and digesting the resulting extract with alcohol, which dissolves a yellow resin, and leaves a white substance to which Payen gives the name of alban. After recrystallisation from absolute alcohol, it forms a white pulverulent mass, which begins to melt at 100°, is perfectly fluid and transparent between 175° and 180°, and contracts strongly in cooling. It dissolves with facility in oil of turpentine, benzol, sulphide of carbon, ether, hot alcohol, and chloroform, and separates from the solutions in the crystalline form. The crystals are wetted by watery liquids. They exhibit with sulphuric acid the same reactions as native gutta percha. (Payen, Compt. rend. xxxv. 109.)

ALBENE. A name given by Völckel to a white substance which, according to his observations, remains undissolved when melam is boiled with water. Völckel assigns to this substance the composition $C^{12}H^9N^{10}O^3$ (Ann. Ch. Phys. [2] lxii. 90).

ALBIN. (See Apophyllite.)

ALBITE. Soda-felspar. (See Felspar.)

ALBUM GRÆCUM. An obsolete name for the excrements of the dog, formerly used as a remedy in medical practice. The substance contains about 79 per cent. of phosphate of calcium.

ALBUMIN. (Gerh. iv. 433; Lehmann, Physiological Chemistry i. 330; also Zoochemie in Gmelin's Handbuch, Bd. viii. Pelouze et Frémy, Traité de Chimie générale, vi. 67.) Albumin is the chief and characteristic constituent of white of egg and of the serum of blood, and occurs in all those animal substances which supply the body or individual parts of it with the materials required for nutrition and renovation. It forms about 7 p. c. of blood and 12 p. c. of white of egg; it is a principal constituent of chyle, lymph and of all serous fluids. It occurs also in the juice of flesh, in the brain, the pancreas, the amniotic liquid, and generally in a greater or smaller quantity in all the liquids (transudates) effused from the blood-vessels into the cellular tissues of the organs, into the cavities of the body, or on to the surface. It is found in the solid excrements of man and of other animals, the quantity increasing in disorders of the mucous membrane of the intestinal canal. It is not found in normal urine, but is present in that liquid in many states of disease, especially in affections of the respiratory organs, which interfere with the process of oxidation.

Albumin exists in two very distinct modifications, viz. the *soluble* form, in which it always occurs in the animal body, and the *insoluble* form, into which it may be brought by the action of heat, as when white of egg or blood-serum is boiled. These two modifications of albumin are identical in chemical composition, the difference between them being due, partly, perhaps, to peculiarity of molecular aggregation, but chiefly to the presence of certain mineral salts which are always associated with the soluble variety. In fact, albumin does not occur in the animal body in the free state, but in the form of an alkaline albuminate; white of egg, serum, and all liquids which contain albumin, leave, when incinerated, an ash chiefly consisting of alkaline carbonate. Insoluble albumin does not appear to exist in the living animal organism, unless indeed, fibrin may be regarded as coagulated albumin, which is by no means improbable, inasmuch as there is no exact method of distinguishing between the two.

Preparation.— Albumin may be prepared either from white of egg, or from blood-serum. White of egg consists of transparent thin-walled cellules, enclosing an alkaline solution of albuminate of sodium. On beating it up with water, the cellular substance separates in pellicles, while the albuminate of sodium remains in solution, together with chloride of sodium and phosphate of calcium. To remove these mineral substances, the liquid, after being filtered from the cellular substance, is mixed with a small quantity of subacetate of lead, which produces an abundant precipitate (an excess of the lead-salt would redissolve it). The mass, after being washed, is stirred up with water to the consistence of a paste, and carbonic acid gas is passed through the liquid. The albuminate of lead is thereby decomposed, carbonate of lead remains suspended in the liquid, and the albumin in the free state remains dissolved. The solution is filtered through paper previously washed with dilute acid, and, as it still retains traces of lead, it is treated with a few drops of aqueous hydrosulphuric acid, and cautiously heated to 60°, till it begins to show turbidity; the first flocks of albumin thus precipitated carry down the whole of the sulphide of lead. When the liquid which after filtration is perfectly colourless, is evaporated in large capsules at 40°, a residue is obtained consisting of pure *soluble* albumin (Wurtz, Ann. Ch. Phys. [3] xii. 27). The same method applied to the albumin of blood-serum does not yield a pure product.

To obtain pure albumin in the coagulated state, white of egg, diluted with an equal bulk of water, filtered, and reduced to its original volume by evaporation at 40°, is mixed with a strong solution of potash, whereby it is soon converted into a translucent, yellowish elastic mass. This is divided into small portions and exhausted with cold water as long as the water removes any alkali, the whole being kept as much as possible from contact with the air. It is then dissolved in water or boiling alcohol, and the solution is precipitated by acetic or phosphoric acid. The precipitate, after washing, leaves no appreciable residue when incinerated. (Lieberkühn.)

Properties.— Soluble albumin, dried in the air, forms a pale yellowish, translucent mass, easily triturated and reduced to a white powder. The specific gravity of the albumin of the hen's egg, from which the salts had not been removed, was found by C. Schmidt (Ann. Ch. Pharm. xi. 156–167), to be 1·3144, and after calculating for the elimination of the salts, the density of pure albumin was found to be 1·2617. It becomes electric by friction, and is tasteless, inodorous and neutral to vegetable colours. It swells in water, assuming a gelatinous appearance; it does not dissolve freely in pure water, but very readily in water containing any alkaline salt. After being dried in vacuo, or at a temperature below 50°, it may be heated to 100° without passing into the insoluble modification. Soluble albumin dried at 60° loses 4 p. c. water at 140°, remaining, however, soluble in water.

The aqueous solution of albumin deviates the plane polarisation of a ray of light to the left. It becomes opaline at 60°, begins to deposit the albumen at 61° to 63°, and at a temperature a little higher the whole coagulates in a mass. When very dilute, it becomes turbid without coagulating; but if the liquid be then concentrated by evaporation, it deposits the albumin in pellicles or flocks.

Coagulated albumin is white, opaque, elastic, and reddens litmus (Hruschauer, Ann. Ch. Pharm. xlvi. 348). When dried, it assumes a yellow colour, and becomes brittle and translucent like horn. When immersed in water, after drying, it gradually absorbs about five times its weight of the liquid, and resumes its primitive consistence.

When coagulated albumin is boiled in *water* for about 60 hours, it gradually disappears, being transformed into a substance soluble in water, and consisting, according to Mulder and Baumhauer (J. pr. Chem. xx. 346; xxxi. 295), of *trioxide of protein*, $C^{40}H^{31}N^{5}O^{8}$ (C = 50·98 p. c.; H = 6·69; O and S = 5·01; N = 27·32). Coagulated albumin, heated to 150° with a small quantity of water in a sealed tube, gradually forms a limpid solution, which has no longer the property of coagulating by heat. (L. Gmelin.)

Albumin is insoluble in *alcohol* and in *ether*. Strong alcohol added in large excess, precipitates albumin from its aqueous solution in the same state as when it is coagulated by heat; but the precipitate produced by a small quantity of weak alcohol redissolves completely in water. When alcohol is added to a somewhat dilute solution of albumin, so as to render it slightly opaline, the liquid after a while, solidifies in a jelly, which, however, is again liquefied by heat. Coagulated serum, or white of egg, may be made to dissolve in alcohol by the addition of a little alkali. (Scherer.)

Ether shaken up with a solution of albumin coagulates but a small portion of it; if, however, the albuminous solution is concentrated, it thickens so much as to appear coagulated. Albumin is not acted upon by oils either fixed or volatile.

Nearly all *acids* precipitate albumin from its solutions. *Nitric acid* precipitates it with peculiar facility, and may therefore be used as a test of the presence of soluble albumin. Strong *hydrochloric acid* aided by heat dissolves coagulated albumin, forming a blue or violet solution, which turns brown when boiled in an open vessel, and according to Bopp (Ann. Ch. Pharm. lxix. 30) yields chloride of ammonium, leucine, tyrosine, and other products of unknown composition. With *aqua regia*, albumin yields both chlorinated and nitro-compounds.

Strong *sulphuric acid* coagulates albumin by the heat which is evolved when the two liquids come in contact. Dilute sulphuric acid precipitates albumin after some time only, not however combining with it, as the acid may be completely removed from the precipitate by washing.

Tribasic phosphoric acid, *acetic*, *tartaric*, and most other organic acids do not form precipitates in moderately concentrated solutions, of albumin; but when either of these acids is added in excess to a highly concentrated solution of serum or white of egg, the liquid solidifies in the cold to a jelly which liquefies like gelatin when heated, and again forms a gelatinous mass on cooling. The aqueous solution of this jelly remains perfectly transparent when boiled, but it is precipitated by a neutral salt of either of the alkali-metals. (Lieberkühn.)

When a small quantity of acetic acid is added to white of egg or serum, so as just to saturate the alkali, and the liquid is then largely diluted with water, flocks of albumin are deposited after awhile. If the supernatant liquid be then decanted, and the precipitate treated with a small quantity of solution of nitre or common salt, it immediately dissolves, and the solution is coagulated by boiling. (Scherer.)

Serum or white of egg mixed with a certain quantity of *common salt* or other salt of an alkali-metal, forms a liquid precipitable by phosphoric, acetic, tartaric, oxalic, lactic acid, &c. Conversely, a solution of albumin (or other albuminoïdal substance) in acetic acid is precipitated by the salts of the alkali-metals. The precipitation is greatly facilitated by heat, and likewise takes place with greater facility as the proportion of salt added is greater. The precipitate dissolves in pure water, with greater facility in proportion as less heat has been applied in producing it; the solution is not coagulated by heat. It is soluble also in acetic acid, phosphoric acid, and even in alcohol, provided it has not been altered by desiccation, or by contact with the air. The aqueous solution is precipitated by certain salts, ferrocyanide of potassium, for example.

Dried soluble albumin suspended in acetic, tartaric, or citric acid, swells up and is converted into coagulated albumin, which may be completely freed from acid by washing. Acetic, tartaric, and tribasic phosphoric acid dissolve coagulated albumin when heated with it. Arsenious acid does not combine with albumin. Chlorine and bromine precipitate albumin.

Alkalis do not in general precipitate albumin from its solutions; but a strong solution of potash added in considerable quantity to a solution of albumin, forms a gelatinous mass of albuminate of potassium. Dilute solutions of potash and soda mix with albumin in all proportions, and on boiling the liquid, an alkaline sulphide is formed. When albumin is heated with hydrate of potassium melted in its water of crystallisation, the water being renewed as it evaporates, ammonia and hydrogen are evolved, leucine and tyrosine are produced, together with oxalate, butyrate valerate, &c. of potassium. *Alkaline carbonates* added to a solution of albumin prevent its coagulation by heat. Coagulated albumin digested at a gentle heat with neutral carbonate or acid carbonate of sodium, displaces the carbonic acid, and forms with the alkali a compound, which, after washing, is perfectly neutral to test paper, but leaves when incinerated a considerable quantity of alkaline carbonate.

Albumin subjected to *dry distillation* yields water, carbonate of ammonium, hydrosulphate of ammonium, volatile alkalis of undetermined composition, empyreumatic oils, &c. Coagulated albumin putrifies when left in contact with water, yielding valeric and butyric acids, a crystalline body having a penetrating odour, an oily acid, and a substance which dissolves in hydrochloric acid, producing a liquid of beautiful violet colour and yielding tyrosine, together with other products (Bopp, Ann. Ch. Pharm. lxix. 30). The *oxygen* of the air has no action on serum or white of egg. Recently extracted serum left for a fortnight in contact with oxygen in a tube standing over mercury absorbs but a very small quantity of the gas, and does not form carbonic acid.

Albumin distilled with a mixture of *peroxide of manganese and sulphuric acid* yields acetic, propionic, butyric, and benzoic aldehydes, together with formic, acetic, butyric, valeric, and benzoic acids, and probably also propionic and caproic acids. Nearly the same products are obtained by distilling albumin with *sulphuric acid and acid chromate of potassium*, this mixture yielding in fact, hydrocyanic acid, a heavy oil having the odour of cinnamon, cyanide of tetryl (valeronitrile), also benzoic, acetic and butyric acids, with small quantities of formic, caproic and propionic acids, and of benzoic and propionic aldehydes (Guckelberger, Ann. Ch. Pharm. lxiv. 39). Albumin does not decompose *oxygenated water*.

Composition of Albumin. — Albumin obtained from various animal fluids exhibits the same composition, as shown by the following analyses: —

	From White of Egg.					
	Mulder.	Scherer.	Dumas and Cahours.	Rüling.	Wurtz.	Lieberkühn.
Carbon	53·4	54·3	53·4	53·4	52·9	53·3
Hydrogen	7·0	7·1	7·1	7·0	7·2	7·1
Nitrogen	15·7	15·9	15·8	..	15·6	15·7
Oxygen	..	..	..	..	..	22·1
Sulphur	..	..	..	1·7 to 1·8	..	1·8

Wurtz's analysis was made with soluble, the rest with coagulated albumin. Mulder supposes that albumin contains also 0·4 per cent. phosphorus. Most of the preparations with which the above analyses were made, contained small quantities of phosphorus in the form of phosphate of calcium.

	From Blood-serum.				
	Dumas and Cahours.		Mulder.	Rüling.	Scherer.
Carbon	53·3	53·5	53·4	53·1	54·5
Hydrogen	7·1	7·3	7·1	7·0	7·0
Nitrogen	15·7	15·8	15·6	..	15·7
Oxygen	..	..	..	..	..
Sulphur	..	..	1·3	1·3	..

Mulder supposes that blood-albumin contains also 0·3 per cent. phosphorus. Rüling found the amount of sulphur in eight analyses to vary from 1·29 to 1·39 per cent.

	Scherer.			Weidenbusch.	Baumhauer.
	a	*b*	*c*	*d*	*e*
Carbon	54·2	54·1	54·0	53·3	54·3
Hydrogen	7·1	7·2	7·0	7·0	7·1
Nitrogen	15·5	15·8	15·8	15·7	15·8
Oxygen	..	..	..	..	..
Sulphur	..	..	..	..	..

a from a hydrocele; *b* from a congestion-abscess; *c* from pus; *d* from flesh of poultry; *e* from the flesh of fish.

From these and other analyses, Liebig deduces the formula $C^{216}H^{339}N^{54}S^{3}O^{68}$: Mulder, $C^{[illegible]}H^{[illegible]}N^{[illegible]}SO^{[illegible]}$: Lieberkühn, $C^{72}H^{112}N^{18}SO^{22}$. Each of these formulæ gives numbers agreeing nearly with the analytical results. Mulder regards albumin as a compound of (hypothetical) protein with (hypothetical) sulphamide, viz.:

$$C^{90}H^{139}N^{22}SO^{30} = \underbrace{5C^{18}H^{27}N^{4}O^{6}}_{\text{Protein.}} + \underbrace{N^{2}H^{4}S}_{\text{Sulphamide.}}$$

Liebig's formula is intended merely to express in a simple form certain relations between albumin and other animal substances. Lieberkühn, on the other hand, regards his formula as actually expressing the composition of the molecule of albumin as it exists in the metallic albuminates (*q. v.*)

According to Lebonte and Goumoens (J. Pharm. [3] xxiv. 17) albumin is not a pure proximate element, but a mixture of two bodies, one of which is insoluble in glacial acetic acid, while the other dissolves in that acid and is precipitated therefrom by potash.

The properties of albumin vary in some degree with the source from which it is derived. The differences may in some cases be attributed to the presence of different mineral substances; but in others they are of such a nature as rather to point to the existence of different modifications of albumin. Thus, Frémy and Valenciennes have found (Ann. Ch. Phys. [3] l. 138) that the albumin of the eggs of certain tribes of birds exhibits peculiar modifications. That from the eggs of different species of gallinaceous birds always exhibits the characters above described; but the eggs of swimming and wading birds yield an albumin which, when diluted with 3 measures of water, is not coagulated by heat, but is precipitated by nitric acid; and the albumin from the eggs of predaceous birds, and of some kinds of perching and climbing birds is neither coagulated by heat nor precipitated by nitric acid. The composition was, however, found to be the same in all cases.

Blood-albumin exhibits the same reactions as that from white of egg, excepting that the latter when boiled gives up part of its sulphur in the form of sulphuretted hydrogen, which blood-albumin does not; nevertheless coagulated white of egg appears to contain more sulphur than blood-albumin.

Paralbumin. — Scherer found in a liquid obtained from a case of ovarian dropsy, a substance resembling albumin, but differing from it in not being completely precipitated by ebullition, even after addition of acetic acid, and in dissolving in water after being precipitated by alcohol. *Metalbumin* is the name given by the same chemist to another supposed modification of albumin, likewise obtained from a pathological fluid, which exhibited similar peculiarities to the preceding, and was further distinguished by giving no precipitate with hydrochloric acid, or with ferrocyanide of potassium after acidulation with acetic acid.

Other substances more or less resembling albumin are: *globulin* or *crystallin* existing in blood-globules and in the crystalline lens of the eye; *hæmatocrystallin*, a crystalline body obtained from blood, and *vitellin*, existing in the yolk of eggs (see these substances).

Quantitative Estimation of Albumin. — The best mode of precipitating albumin from alkaline liquids (serum, for example), for quantitative estimation, is to neutralise or slightly acidulate the liquid with acetic acid, and then coagulate the albumin by boiling. The precipitate thus obtained is flocculent and may be easily collected on a filter and washed, the liquid passing through perfectly clear, whereas if the albumin be coagulated by heat alone, it is very apt to clog the filter. Another reason for using the acetic acid is, that mere boiling does not precipitate the albumin completely from alkaline solutions. The precipitated albumin, after being thoroughly washed, may be dried in vacuo over sulphuric acid or in a current of warm air.

Uses of Albumin.— Albumin is much used for clarifying vinous and syrupy liquids, inasmuch as, when boiled with them, it coagulates, and takes hold of the colouring matter and other impurities, thereby removing them, and carrying them to the bottom or to the surface of the liquid, according to its density. In cookery, white of egg is employed for this purpose, but in large operations, such as sugar-refining, the serum of blood is used. Albumin is applied to a considerable extent for fixing colours in calico-printing; it is also used in photography. Its property of forming a hard compound with lime renders it very useful for making cement for laboratory purposes and for mending broken earthenware. A paste made of white of egg and slaked lime, acquires after a while the hardness of stone.

ALBUMINATES. (Lassaigne, Ann. Ch. Phys. [3] lxiv. 90; Lieberkühn, J. Pharm. [3] xxxiii. 398; Lehmann, Physiol. Chem. i. 332; Gerh. iv. 447.) — Albumin is a weak acid, and apparently dibasic. Its compounds with the alkalis are soluble and are obtained directly by treating albumin with caustic alkalis or alkaline carbonates. The other albuminates are insoluble and are obtained by precipitation.

Albuminate of Barium, $C^{72}H^{111}BaN^{18}SO^{22} + H^{2}O$ (?) — A solution of albuminate of potassium in dilute alcohol forms with barium-salts, a precipitate which dries up to a white powder, insoluble in water, alcohol and ether. White of egg mixed with caustic baryta, strontia or lime, forms an insoluble compound, which becomes very hard when dry.

Albuminate of Copper, $C^{72}H^{110}Cu^2N^{18}SO^{22} + H^2O$ (?) — Obtained in like manner forms when dry, a green, brittle mass, insoluble in water and alcohol. Acids decolorise, but do not dissolve it (Lieberkühn). According to Lassaigne, double albuminates of copper with potassium, or barium, or calcium, may be obtained by heating hydrate of copper with solution of albumin and solution of potash, baryta or lime. There is also an albuminate of copper and magnesium which is insoluble and has a lilac colour.

Albuminate of Lead is a white insoluble salt, obtained by mixing the solution of albumin and subacetate of lead; it is soluble in excess of the lead-salt, and is decomposed by all acids.

Mercuric Albuminate is a white substance obtained by precipitating corrosive sublimate with albuminate of sodium (white of egg). It is insoluble in pure water, but soluble in saline liquids; for this reason, when white of egg is used as an antidote in cases of poisoning by corrosive sublimate, endeavours should always be made to produce vomiting; otherwise a portion of the mercuric albuminate may remain dissolved in the gastric juice, which contains chloride of sodium.

Albuminate of Potassium, $C^{72}H^{110}K^2N^{18}SO^{22} + H^2O$. — Prepared by mixing a concentrated solution of white of egg with strong potash-ley, and washing the resulting gelatinous mass with cold water, as long as any alkali dissolves out, then dissolving the residue in boiling alcohol, and precipitating by ether. After drying, it is no longer soluble in boiling alcohol or in water. The aqueous solution is not coagulated by boiling or by addition of alcohol. With a small quantity of acetic, tartaric, citric or phosphoric acid, it yields an abundant white precipitate easily soluble in excess of acid. These characters are the same as those of casein; hence, Gerhardt considers it probable that casein may be really albuminate of potassium.

Albuminate of Sodium is contained in blood-serum and in white of egg, together with chloride of sodium and phosphate of calcium. Serum and white of egg have a slight alkaline reaction, are more soluble in water than pure albumin, and when boiled, coagulate in a gelatinous mass, not in flakes. After boiling, the filtered liquid is more alkaline than before, and still contains albuminate of sodium, whereas the coagulum is free from alkali. Hence, Gerhardt thinks it probable that serum and white of egg contain an acid albuminate of sodium, $C^{72}H^{111}NaN^{18}SO^{22}$, which is decomposed by heat into the neutral albuminate, and free albumin which separates from the liquid. This view is, moreover, in accordance with the composition of dried white of egg, which, according to Lehmann's analysis, contains 1·6 per cent. of soda, the formula $C^{72}H^{111}NaN^{18}SO^{22} + H^2O$ requiring 1·8 per cent. White of egg or serum treated with strong caustic soda, yields a gelatinous mass nearly insoluble in cold water, and closely resembling the compound produced under the same circumstances by potash. This gelatinous salt appears to be the neutral *albuminate of sodium*, $C^{72}H^{110}Na^2N^{18}SO^{22} + H^2O$. It contains, according to Lehmann, 3·14 per cent. soda (by calculation 3·7).

Albuminate of Silver, $C^{72}H^{110}Ag^2N^{18}SO^{22} + H^2O$ (?) — Obtained by precipitation. White, flocculent, blackens when exposed to light.

Albuminate of Zinc, $C^{72}H^{110}Zn^2N^{18}SO^{22} + H^2O$ (?)—White powder insoluble in water, alcohol, and ether.

ALBUMIN, VEGETABLE. (Gerh. iv. 444; Handw. d. Chem 2te Aufl. ii. 147.) — Most vegetable juices contain a substance which appears to be identical in composition and properties with the albumin of blood or of white of egg. The same compound appears also to exist in the solid form in certain parts of plants, especially in the seed. Vegetable juices containing albumin deposit it, when heated to 65° or 70°, in flocks, which are often coloured greenish by chlorophyll, and contain fatty and waxy substances mechanically enclosed. To remove these matters, the coagulum must be washed, first with water, then with boiling alcohol and with ether.

Albumin is especially abundant in the juice of carrots, turnips, cabbages, and the green stems of peas, but it is more easily prepared from potatoes, by cutting them into slices, covering them with very dilute sulphuric acid (of 2 p.c.), leaving the liquid to itself for 24 hours, then adding fresh potatoes, and repeating the same operation once more, afterwards neutralising the solution with potash, and boiling. A considerable quantity of albumin is then deposited in thick white flocks.

Wheat-flour also contains a considerable quantity of albumin, which may be extracted with cold water. For this purpose, the water which runs off in washing the paste of wheat-flour for the preparation of gluten (*q. v.*) is left at rest till the starch is completely deposited; the clear liquid is then heated to the boiling point, whereupon it deposits a small quantity of albumin; on evaporating the solution a larger quantity is obtained.

Oleaginous seeds likewise contain albumin, which may be extracted by beating the seeds with water into an emulsion, extracting the fat by agitation with ether, and the albumin by boiling.

When sweet almonds which have been freed from their envelopes are reduced to a pulp by rasping, and the pulp is digested for a few minutes in boiling water, the sugar, gum, and the greater part of the legumin contained in the almonds enter into solution; and on depriving the residue of fatty matter by means of ether, nothing is left but coagulated albumin, exhibiting the same characters as coagulated white of egg.

	a	*b*	*c*		*d*	*e*	*f*	*g*
Carbon	54·0	53·7	51·9 to	52·0	53·1	52·0		
Hydrogen	7·8	7·1	6·9	7·0	7·2	6·8		
Nitrogen	15·8	15·7	18·4	..	..	..		
Oxygen	..	..	..	..	..	..		
Sulphur	..	..	..	..	0·97	0·79	1·0	0·77

a, albumin from rye, analysed by Jones (Ann. Ch. Pharm. xl. 66); *b*, from wheat-flour, by Dumas and Cahours (Ann. Ch. Phys. [3] vi. 309); *c*, from wheat-flour by Boussingault (ibid. [2] lxiii. 225); *d*, from potatoes by Rüling (Ann. Ch. Pharm. lviii. 306); *e*, from peas by Rüling; *f*, *g*, from rye, by Mulder.

Vegetable albumin is distinguished from legumin (vegetable casein) by being coagulated by heat, and not precipitated by acetic acid. It exhibits the same reactions as animal albumin with acids, alkalis, tannin, chloride of mercury, &c. The mode of its occurrence differs, however, remarkably from that of animal albumin in this respect, that it is always found in plants in neutral or acid liquids, whereas animal albumin exists only in alkaline liquids (p. 25).

The albumin of sweet almonds is remarkable for the facility with which it decomposes, and by its property of acting as a ferment, and determining the metamorphosis of amygdalin, salicin, and other organic bodies. This altered albumin is distinguished by the terms *emulsion* and *synaptase* (*q. v.*)

The *myrosin* of mustard-seeds likewise resembles vegetable albumin. Lastly, the *diastase* of germinated barley, *beer-yeast*, and *wine-lees* are likewise albuminoïdal substances in a state of alteration.

ALBUMININ. *Oonin.* (Handw. d. Chem. 2^{te} Aufl. i. 404.)—The name given by Couerbe to the substance of the cells which enclose the white of birds' eggs. It is obtained by exposing white of egg for a month to temperature between 0° and—8°, in the form of a white filmy substance, which when dried is white, translucent in thin laminæ and easily friable. It does not contain nitrogen, and consequently does not evolve ammonia when heated. It is insoluble in water, whether hot or cold, but swells up in hot water, forming a gummy mass. It is not acted upon by alcohol, ether, or acetic acid. Nitric and sulphuric acids decompose it. It dissolves in hydrochloric acid, and on adding water to the solution, a white powder is precipitated. It dissolves in caustic potash, forming a solution which is rendered turbid by acids, but not precipitated.

ALBUMINOÏDS. *Protein-compounds. Blutbilder.* (Gerh. iv. 430; Handw. d. Chem. 2^{te} Aufl. ii. 120.) — This term is applied to a class of compounds which play an important part in the functions of animal and vegetable life. Three of them, *albumin*, *casein*, and *fibrin* are distinguished by well-marked characters.

Fibrin separates spontaneously in the solid form from blood, soon after its removal from the living body; albumin is contained in the serum or more liquid portion of the blood, and separates from it as a coagulum on the application of heat; and casein is contained in milk, from which it may be separated, not by heat, but by the addition of an acid. The same substances are found in plants, viz. fibrin, in the grain of wheat and other cereal plants; albumin in most vegetable juices, and casein (or legumin) in the seeds of the pea, bean and other leguminous plants.

The other bodies of this class are less distinctly characterised; indeed, most of them appear to be mere modifications of the one or other three above-mentioned: thus, *syntonin*, the essential constituent of the muscular fibre, closely resembles blood-fibrin; *vitellin*, a substance occurring in the yolk of eggs, is scarcely distinguishable from albumin; and *globulin* and *hæmatocrystallin*, two substances contained in the blood, resemble albumin in the property of coagulating by heat.

Moreover, albumin, fibrin, and casein, though clearly distinguished from one another by the different conditions under which they pass from the liquid to the solid state, nevertheless possess many characters in common. They all dissolve in caustic potash or soda, and when boiled with those alkalis, yield solutions from which acids precipitate them in a more or less altered state, and at the same time eliminate hydrosulphuric acid. When subjected to dry distillation, they all give off ammonia (or compound ammonias). They all decompose and putrefy with great facility when exposed to moist air, and in that form are very active as *ferments;* thus, yeast, wine-lees, diastase, &c., are merely albuminoïdal substances in a peculiar state of decomposition.

All albuminoïds treated with oxidising agents, such as mixtures of peroxide of manganese or acid chromate of potassium and sulphuric acid, yield the same products, viz. acids and aldehydes of the acetic and benzoic series (see ALBUMIN, p. 67).—Albuminoïds dissolve in very strong hydrochloric acid, forming a solution which is yellow if kept from contact with the air, but assumes a fine blue or violet colour on exposure to the air.—A solution of mercury in an equal weight of nitric acid imparts to these bodies a very deep red colour, this test serving to detect the presence of 1 part of albumin in 100,000 parts of water.

All the albuminoïds exhibit the same or nearly the same constitution. In the living organism, albumin, fibrin, and casein are constantly being converted one into the other. The casein of milk supplies the material for the formation of albumin and fibrin; and conversely, albumin and fibrin are converted into casein. Indeed, the analyses of different bodies of the class do not differ from one another more than analyses of the same body from different sources or by different experimenters. They contain 50 to 54 p. c. carbon, about 7 p. c. hydrogen, 15 to 17 p.c. nitrogen, about 25 p. c. oxygen, and from 0·9 to 1·8 sulphur. According to some analyses, however, fibrin contains rather less carbon and more nitrogen than albumin. Albumin and fibrin have been supposed by some chemists to contain also a small quantity of phosphorus as an organic constituent, but its existence is not well established. Most albuminoids are associated with small quantities of mineral substances, including phosphate of calcium, which cannot be separated from the organic matter by acids.

This great similarity of composition and properties exhibited by these bodies has led to various views of the relation between them. Mulder supposed that all the albuminoïds contain the same organic group, $C^{18}H^{27}N^{4}O^{6}$, which he called *protein,* combined with different quantities of sulphur and phosphorus, and that the conversion of one of these bodies into the other depends upon the assumption or elimination of small quantities of one or both of those elements (see PROTEIN). Mulder also stated, that when an albuminoïd is treated with caustic alkali, the sulphur and phosphorus are removed and the protein remains. The researches of other chemists have shown, however, that this view is untenable. Neither of the albuminoïds contains phosphorus, and the proportion of sulphur appears to be the same in them all: at all events, fibrin and egg-albumin, which perhaps exhibit the greatest difference of physical and chemical properties, do not differ perceptibly in amount of sulphur. Moreover, the sulphur of albuminoïds cannot be completely extracted by the action of alkalis, so that the existence of the so-called protein is merely hypothetical.

Gerhardt was of opinion that all the albuminoïds are identical, not only in composition, but in chemical constitution, and that they differ from one another only in molecular arrangement, and by the nature of the mineral substances with which they are associated; in fact, that they contain a common proximate element which, like many other organic compounds, is capable of existing in a soluble and in an insoluble modification. Designating this common element by the name albumin, he supposed that white of egg and serum consist of acid albuminate of sodium (p. 99), which is separated by heat into free albumin and neutral albuminate of sodium, the latter remaining dissolved; that casein, which is soluble and non-coagulated by heat, consists of neutral albuminate of potassium, from which the organic compound may be precipitated by neutralising the alkali with an acid; and that fibrin is albumin in the insoluble state, more or less mixed with earthy phosphates. This view is in accordance with the fact that fibrin and casein may be dissolved in neutral potassium-salts (better with addition of a little caustic alkali), forming a liquid which coagulates by heat, and deflects the plane of polarisation of a luminous ray to the left, like albumin; and that fibrin and albumin, dissolved in a certain quantity of caustic alkali, exhibit the characters of soluble casein. Nevertheless, it is possible to obtain the albuminoïds in some cases wholly, in others very nearly, free from mineral matters, and nevertheless exhibiting their distinguishing characteristics. Moreover, it is certain that all these bodies contain the same proportions of carbon, nitrogen, and sulphur.

Strecker (Handw. d. Chem. 2te Aufl. ii. 124) supposes the albuminoïds to be composed of a great number of radicles (a supposition in accordance with the variety of their products of decomposition); that the greater number of these radicles are the same in all — hence their great similarity, — but that each contains one or more such radicles peculiar to itself. Thus, when casein is converted in the animal body into albumin and fibrin, it may take the radicles required for that transformation from the other constituents of the milk, viz. the fat and the sugar. (See Albumin, Blood, Casein, Crystalline, Fibrin, Globulin, Hæmatocrystallin, Legumin, Milk, Vitellin.)

ALBUMINOSE. This term is applied by Bouchardat to a product of the decomposition of animal fibrin by very dilute hydrochloric acid (see Fibrin), and by Mialhe, to a peculiar substance into which he supposes albumin to be converted by the action of the gastric juice before it is assimilated.

ALCARRAZAS. Very porous vessels of slightly burnt clay used in hot climates for cooling water and other liquids. The liquid oozes through the pores and stands on the outside of the vessel in a sort of dew, which rapidly evaporates, especially if the vessel is exposed to a current of air, and thereby cools the liquid.

ALCHEMILLA VULGARIS. 100 pts. of the fresh plant contain, according to Sprengel: 76·0 pts. water, 10·3 pts. extractable by water, and 7·8 by dilute potash-ley; 5·6 woody fibre and 1·66 ash free from carbonic acid. The ash contained in 100 pts.; 30·5 potash, 2·4 soda, 33·6 lime, 4·9 magnesia, 0·9 alumina, 14·4 silica, 4·4 sulphuric anhydride, 5·4 phosphoric anhydride, 3·5 chlorine, and traces of the oxides of iron and manganese.

ALCOHOL. $C^2H^6O = C^2H^5.H.O$ [or $C^4H^6O^2 = C^4H^5O.HO.$]. This compound, which is the spirituous or intoxicating principle of wine, beer, and other fermented liquors, may be regarded as the hydrate or hydrated oxide of ethyl, or as a molecule of water, HHO, in which half the hydrogen is replaced by the radicle *ethyl*, C^2H^5. It has also been regarded as a compound of ethylene and water, $C^2H^4.H^2O$.

History.— Intoxicating drinks produced by fermentation of vegetable juices containing sugar, have been known from the earliest times; but it was not till the twelfth century that the method of obtaining pure spirit of wine or hydrated alcohol from these liquids by distillation, was discovered by Abucasis; and the dehydration of this liquid was first partially effected by means of carbonate of potassium by Raimond Lullius in the thirteenth century. The mode of obtaining perfectly anhydrous alcohol was afterwards discovered by Lowitz.

Formation.—1. By the decomposition of glucose (grape-sugar) under the influence of ferments, that is to say, of nitrogenous organic substances, such as yeast, which are themselves undergoing decomposition. The sugar is then resolved into alcohol and carbonic anhydride:

$$C^6H^{12}O^6 = 2C^2H^6O + 2CO^2.$$

Other kinds of sugar, cane-sugar for example, as well as starch, woody fibre and other vegetable substances, also yield alcohol under the influence of ferments, but they are first converted into glucose.

2. From ethylene or olefiant gas, by addition of the elements of water:

$$C^2H^4 + H^2O = C^2H^6O.$$

Olefiant gas briskly agitated for a long time with strong sulphuric acid, is absorbed, and on diluting the liquid with water and distilling, alcohol passes over. This mode of formation, first observed by Hennel (Phil. Trans. 1826, p. 240), has lately been confirmed and fully examined by Berthelot (Ann. Ch. Phys. [3] xliii. 385). As olefiant gas can be obtained from inorganic materials, it follows that alcohol may be produced without the agency of living organisms.

Preparation. 1. *Of Hydrated or Aqueous Alcohol.*—When wine and other liquids which have undergone the vinous fermentation are distilled, alcohol passes over together with a considerable quantity of water; and by subjecting the product to repeated distillations, spirit is obtained continually richer in alcohol, because the alcohol, being more volatile than the water, passes over in larger quantity than the latter. But it is not possible to remove the whole of the water by simple distillation. The residue of the distillation, if continued long enough, is nothing but water containing small quantities of acetic acid (produced by oxidation of the alcohol) and fusel oil. Portions of these impurities also pass into the rectified spirit. The greater part of the acetic acid however, and a considerable portion of the fusel oil are left in the residues of the several distillations. The last portion of the acid is easily removed by distillation over a small quantity of carbonate of potassium or wood-ashes: and the fusel oil, which adheres more obstinately, and imparts a very unpleasant odour to the spirit, is best removed by adding to the spirit about 0·7 of its weight of coarsely powdered charcoal, leaving the mixture to stand for several days, and stirring it repeatedly, then decanting and distilling. Bone-black or blood-charcoal may also be used.

2. *Of Anhydrous or Absolute Alcohol.*—Alcohol cannot be completely dehydrated by distillation, because, at the boiling-point of pure alcohol (78° C.), the vapour of water possesses a considerable tension. The most highly rectified spirit obtained by frac-

tional distillation, still retains about 9 per cent. of water. The last portions of water must be removed by the agency of some substance which has a powerful attraction for it. Carbonate of potassium, chloride of calcium, and quick lime, are the substances most commonly used for this purpose, more rarely acetate of potassium, sulphate of copper, and other salts.

a. By *Carbonate of Potassium.*—Highly rectified spirit is shaken up with ignited carbonate of potassium, which forms a watery or pasty layer at the bottom. The alcohol, whose density is thereby lowered to 0·815, is poured off into a distilling vessel containing twice the quantity of pulverised and recently ignited carbonate of potassium, left to stand for 24 hours, and then two-thirds of it are distilled off (Lowitz). This method does not however remove the last minute portions of water.—*b.* A more complete dehydration is effected by *chloride of calcium.* The salt fused or dehydrated by a heat of 400° C. is added in thick lumps to twice its weight of spirit containing 90 per cent. of real alcohol; and the mixture left for some days in a closed vessel and occasionally shaken up, after which it is distilled in a retort over a fresh quantity of fused chloride of calcium. The retort is heated in a sand or oil bath with its neck directed upwards to prevent the contents from spirting over. When the quantity of alcohol is large, a second treatment with chloride of calcium is necessary to effect complete dehydration.

c. By *Quick lime.*—A retort is two-thirds filled with small pieces of quick lime, and a quantity of 90 per cent. spirit poured in sufficient to nearly cover the lime. The lime soon slakes and becomes heated; the mixture is left to digest for some hours; and the anhydrous alcohol is then distilled off in the water-bath. The distillation must be carefully conducted, otherwise the distillate will be contaminated with lime. Alcohol containing fusel oil acquires a very unpleasant odour when treated with lime. This is by far the easiest method of obtaining absolute alcohol.

d. When aqueous alcohol is enclosed in a bladder, and exposed to warm air, the water gradually percolates through the bladder and evaporates, and absolute alcohol is left inside. (Sömmering.)

Alcohol may be regarded as anhydrous if sulphate of copper previously burnt white does not acquire any blue colour when immersed in the alcohol in a close vessel (Cassoria), or if it forms a perfectly clear mixture with benzol (Görgeu). It is doubtful however whether either of these tests will indicate the presence of a very minute quantity of water.

Properties.—Alcohol is a transparent, colourless, very mobile liquid, having a strong refracting power. Its specific gravity, according to Kopp (Pogg. Ann. lxxii. 1), is 0·792 at 20°; or 0·7939 at 15·5°, or 0·8095 at 0°. If its volume at 0° C. be taken for unity, the volume at any temperature t° is given by the formula:

$$v = 1 + 0{\cdot}001041139t + 0{\cdot}0000007836t^2 + 0{\cdot}000000017618t^3.$$

and therefore for the temperatures:

0° C.	5° C.	10° C.	15° C.	20° C.	25° C.	30° C.
1·00000	1·00523	1·01052	1·01585	1·02128	1·02680	1·03242

the volumes of a given quantity of alcohol are as the numbers (second row above).

Alcohol has never been reduced to the solid state, but becomes viscid at very low temperatures, as when it is surrounded with a mixture of solid carbonic acid and ether under an exhausted receiver. It boils at 78·4° C. (173·1° Fah.) when the barometer stands at 0·76 met. (Gay-Lussac, Kopp.) Vapour-density = 1·613 (Gay-Lussac); by calculation, for a condensation to 2 volumes, it is 1·591 when referred to air as unity, and 23 when referred to hydrogen as unity $\left(\frac{2 \times 12 + 6 \times 1 + 16}{2} = 23.\right)$ Alcohol has an enlivening odour and a burning taste, and when unmixed with water exerts a poisonous action. It is a very slow conductor of electricity.

Decompositions. 1. *By Heat.*—Alcohol-vapour passed through a red-hot glass or porcelain tube yields carbonic anhydride, water, hydrogen, marsh-gas, olefiant gas, naphthalin, empyreumatic oil and a deposit of charcoal. If the tube be filled with fragments of pumice-stone, the solid and liquid products consist of nalphthalin, benzol, hydrate of phenyl, acetic acid (?) and aldehyde, together with a number of solid compounds of not very definite character, some of them smelling like musk, others like garlic (Berthelot, Ann. Ch. Phys. [3] xxxiii. 285). Alcohol-vapour does not undergo decomposition at 300° C. in a tube containing fragments of porcelain, but gives off gas even at 220°, if the tube contains spongy platinum. (Reiset and Millon, Ann. Ch. Phys. [3] viii. 280.)

2. *By Electricity.*—Absolute alcohol scarcely conducts the voltaic current, but when potash or potassium is dissolved in it, decomposition takes place, hydrogen being

evolved at the negative pole and aldehyde-resin formed at the positive pole. (Connell.)

3. *By Oxygen.* — Alcohol is very inflammable, and burns in the air with a dull blue flame, yielding water and carbonic acid. It does not readily deposit soot, even when the supply of air is limited, but absolute alcohol deposits it more readily than ordinary spirit. Alcohol-vapour mixed with air explodes by contact with flame or by the electric spark.

Imperfect Combustion. — When alcohol or its vapour comes in contact with air, and at the same time with platinum or certain other metals, an imperfect oxidation of the alcohol takes place, the metal being generally heated to redness, and the alcohol being converted, partly into carbonic acid and water, partly into aldehyde, acetic acid, formic acid, acetal, and a peculiar compound having an excessively pungent odour. Some metals excite this action at ordinary temperatures, others only when more or less heated; but in all cases the action is more powerful as the metal is more finely divided and consequently exposes a larger surface to the alcohol-vapour. The most powerful action is exerted by *platinum black.* When this substance is shaken on paper moistened with alcohol, it makes a hissing noise and becomes red-hot, sometimes setting fire to the alcohol, or else continuing to glow, and inducing the slow combustion above mentioned. If the platinum be previously moistened with a small quantity of water, or at once covered completely with alcohol, the ignition is prevented, and the slow combustion induced with greater certainty. If a number of watch-glasses containing moist platinum black, be placed above a dish containing alcohol, and a bell jar open at top inverted over them, the alcohol turns sour in a few weeks, and is found to contain aldehyde, acetal, acetic acid, and acetic ether.

This action of platinum black affords an excellent means of discovering the presence of alcohol in the air or in watery liquids. The liquid, neutralised, if necessary, with alkali, to prevent the escape of volatile acids, is introduced into a retort, into the neck of which, and near the bulb, is thrust a little boat containing platinum black, and on each side of this boat is placed a piece of litmus paper, in contact with the platinum. The retort is then gently heated in the water-bath, when, if alcohol is present, its vapour will be converted into acetic acid by contact with the platinum black and the paper will be reddened (Buchheim). [Other volatile organic liquids might exert a similar action.]

Spongy platinum and clean platinum wire act in a similar manner to platinum black, but not so quickly. If a coil of platinum wire be placed round the wick of a spirit-lamp, the alcohol set on fire till the wire becomes red-hot, and the flame then blown out, the wire will continue to glow and the alcohol-vapour to burn slowly, producing acetic acid, aldehyde, &c. The same effect is produced by a ball of spongy platinum. This is the *lamp without flame*, or *glow lamp* of Sir H. Davy.

4. *By Chlorine.* — Chlorine gas is rapidly absorbed by alcohol, imparting to it a yellow colour and causing considerable rise of temperature, which, if the liquid is exposed to light, may even cause it to take fire. At the same time it rapidly abstracts hydrogen, which is partly replaced by chlorine, thereby producing hydrochloric acid, aldehyde, acetal, acetic acid, acetate of ethyl, chloride of ethyl, and finally chloral. The mixture of these substances, freed by washing with water from the soluble constituents, was formerly called *heavy hydrochloric ether.* The formation of these several products is represented by the following equations:

$$\underbrace{C^2H^6O}_{\text{Alcohol.}} + 2\,Cl = \underbrace{C^2H^4O}_{\text{Aldehyde.}} + 2\,HCl$$

$$\underbrace{C^2H^4O}_{\text{Aldehyde.}} + 6\,Cl = \underbrace{C^2HCl^3O}_{\text{Chloral.}} + 3\,HCl$$

$$\underbrace{C^2H^6O}_{\text{Alcohol.}} + HCl = \underbrace{C^2H^5Cl}_{\substack{\text{Chloride of}\\ \text{ethyl.}}} + H^2O$$

$$\underbrace{C^2H^6O}_{\text{Alcohol.}} + H^2O + 4\,Cl = \underbrace{C^2H^4O^2}_{\text{Acetic acid.}} + 4HCl$$

$$\underbrace{C^2H^6O}_{\text{Alcohol.}} + \underbrace{C^2H^4O^2}_{\text{Acetic acid.}} = \underbrace{C^2H^3O^2.C^2H^5}_{\text{Acetate of ethyl.}} + H^2O$$

Acetate of ethyl may also be formed by the direct action of chlorine on the alcohol; thus:

$$2\,C^2H^6O + 4Cl = C^2H^3O^2.C^2H^5 + 4\,HCl$$

The acetal, which is probably formed at the beginning of the process, according to the equation:

$$3C^2H^6O + 2\,Cl = C^6H^{14}O^2 + H^2O + 2HCl,$$

is for the most part subsequently converted into acetic acid:

$$C^6H^{14}O^2 + 4H^2O + 10Cl = 3C^2H^4O^2 + 10HCl.$$

When the action of the chlorine is continued for a long time, chloral is always the principal product.

Chlorine in presence of alkalis, converts alcohol into chloroform and carbonic anhydride:

$$C^2H^6O + 8Cl + O = CHCl^3 + 5HCl + CO^2.$$

The same products are formed by distilling dilute alcohol with hypochlorite of calcium (chloride of lime, bleaching powder). (See CHLOROFORM.)

Bromine acts upon alcohol in a similar manner to chlorine, producing bromal, hydrobromic acid, bromide of ethyl, bromide of carbon, formic acid, and other products not yet thoroughly examined. *Iodine* is at first dissolved by alcohol without decomposition, and forms a brown solution; but after a while, hydriodic acid is produced, and acting upon a portion of the alcohol, forms iodide of ethyl. An alcoholic solution of potash treated with iodine yields iodoform and iodide of potassium, the former of which compounds may be separated by water.

9. *Chloric acid*, in the concentrated state, sets fire to alcohol; when diluted, it forms acetic acid, the action being sometimes attended with evolution of chlorine. *Perchloric acid* mixes with alcohol without decomposition at ordinary temperatures, but the liquid when heated first gives off alcohol, then ether, and ultimately white vapours smelling like oil of wine, the residue at the same time turning black.

10. *Strong Nitric acid* decomposes alcohol, with great evolution of heat and brisk ebullition, a mixture of various elastic fluids, the *ethereal nitrous gas* of the older chemists, being evolved and an acid liquid remaining behind; if the nitric acid is dilute, the action does not take place without application of heat. Part of the nitric acid unites directly with the alcohol, forming nitrate of ethyl, but the greater part is reduced to nitrous acid which then forms nitrite of ethyl (nitrous ether) with a portion of the alcohol, while the remainder of the alcohol is oxidised and converted into aldehyde, acetic acid, formic acid, saccharic acid, oxalic acid, glyoxal, glyoxylic acid, and glycollic acid, together with water and carbonic anhydride, which escapes as gas, together with nitric oxide and the vapours of the more volatile among the compounds just mentioned. The formation of glyoxal, glyoxylic acid, and glycollic acids is represented by the equations:

$$\underbrace{C^2H^6O}_{\text{Alcohol.}} + 3O = \underbrace{C^2H^2O^2}_{\text{Glyoxal.}} + 2H^2O$$

$$\underbrace{C^2H^6O}_{\text{Alcohol.}} + 3O = \underbrace{C^2H^4O^3}_{\text{Glycollic acid.}} + H^2O$$

$$\underbrace{C^2H^2O^2}_{\text{Glyoxal.}} + O + H^2O = \underbrace{C^2H^4O^4}_{\text{Glyoxylic acid.}}$$

If urea be added to the mixture of nitric acid and alcohol so as to decompose the nitrous acid as fast as it is formed (see UREA), the chief product of the action is nitrate of ethyl $NO^3.C^2H^5$. Hydrocyanic acid has also been observed among the products of the action of nitric acid upon alcohol.

When strong alcohol is heated with red fuming nitric acid (containing nitrous acid) and nitrate of silver or mercuric nitrate is added, white fumes are given off, containing aldehyde and other oxidised products, and a crystalline deposit of fulminate of silver or mercury is formed, its production being due to the action of the nitrous acid on the alcohol: *e.g.*

$$\underbrace{C^2H^6O}_{\text{Alcohol.}} + 2\,\underbrace{NO^2Hg}_{\text{Mercuric nitrite.}} = \underbrace{C^2N^2Hg^2O^2}_{\text{Fulminate of mercury.}} + 3\,H^2O$$

But when a solution of mercury in nitric acid free from nitrous acid is added at a temperature below 100° C. to alcohol of sp. gr. 0.844, no action takes place at first; but on raising the temperature to 100°, a white crystalline precipitate is formed, which is a compound of mercuric nitrate with a nitrate of ethyl in which the whole of the hydrogen is replaced by mercury (Sobrero and Selmi; Gerhardt):

$$2\,NO^3H + 3\,Hg^2O + C^2H^6O = \underbrace{NO^3Hg.NO^3(C^2Hg^5) + H^2O}_{\text{Crystalline compound.}} + 3\,H^2O$$

11. *Sulphuric acid* forms with alcohol, a number of products varying in quantity according to the proportions in which the two liquids are mixed, their degree of concentration, and the temperature to which the mixture is exposed.

Strong sulphuric acid mixes with alcohol, producing considerable evolution of heat, and forms ethyl-sulphuric or sulphovinic acid, the acid being at the same time brought to a greater state of dilution:

$$\underbrace{C^2H^5.H.O}_{\text{Alcohol.}} + SO^4.H^2 = \underbrace{SO^4.H.C^2H^5}_{\text{Ethyl-sulphuric acid.}} + H^2O$$

When the strongest sulphuric acid (sp. gr. 1·825) is digested for some time at a gentle heat, with excess of absolute alcohol, more than half the sulphuric acid is converted into ethyl-sulphuric acid. If the acid or the alcohol is diluted with water, a considerable quantity of the sulphuric acid remains unaltered. Sulphuric acid containing 1 at. water ($SO^4H^2.H^2O$) forms ethyl-sulphuric acid only when heated. As the formation of ethyl-sulphuric acid is necessarily accompanied by that of water, a certain portion of the sulphuric acid must always remain unconverted into ethyl-sulphuric acid.

Formation of Ether.—A mixture of 1 pt. alcohol, and from 1 to 2 pts. strong sulphuric acid heated in a distillatory apparatus, boils between 120° and 140° C., at first giving off ether, together with more or less undecomposed alcohol, then at 140° scarcely anything but ether, at 160° ether and water,—and at length when, in consequence of the decomposition of the alcohol, the proportion of sulphuric acid has become excessive, and the temperature rises above 160°, the mixture blackens and gives off olefiant gas together with sulphurous acid and other products hereafter to be mentioned. If however the alcohol be allowed to flow constantly into the vessel in a thin stream, so as to maintain the proportion of 5 pts. alcohol to 9 pts. sulphuric acid, the temperature remains constant at about 140°, no sulphurous acid or olefiant gas is formed, but the alcohol, as fast as it is supplied, is given off again in the form of ether and water.

The alcohol converts a molecule of sulphuric acid into ethyl-sulphuric acid and water, as above:

$$\underbrace{C^2H^5.H.O}_{\text{Alcohol.}} + \underbrace{SO^4.H^2}_{\text{Sulphuric acid.}} = \underbrace{SO^4.C^2H^5.H}_{\text{Ethyl-sulphuric acid.}} + \underbrace{H^2O}_{\text{Water.}}$$

and the ethyl-sulphuric acid coming in contact with another molecule of alcohol, yields ether and sulphuric acid:

$$\underbrace{SO^4.C^2H^5.H}_{\text{Ethyl-sulphuric acid.}} + \underbrace{C^2H^5.H.O}_{\text{Alcohol.}} = \underbrace{(C^2H^5)^2O}_{\text{Ether.}} + \underbrace{SO^4H^2}_{\text{Sulphuric acid.}}.$$

The sulphuric acid thus reproduced acts in like manner upon another molecule of alcohol, and in this way the process continues as long as the supply of alcohol is kept up. Etherification is therefore a continuous process, a given quantity of sulphuric acid being capable of etherifying a very large quantity of alcohol. The water, however does not all pass off as it is formed, so that the sulphuric acid becomes continually though slowly weaker, and consequently a continually larger quantity of alcohol passes over undecomposed with the ether and water.

The explanation just given of the process of etherification is due to Williamson (Chem. Soc. Qu. J. iv. 106, 229). Its correctness is strikingly exhibited by the analogous reaction which takes place between common alcohol and amyl-sulphuric acid. When amyl-alcohol is dissolved in sulphuric acid, amyl-sulphuric acid is produced:

$$C^5H^{11}.H.O + SO^4H^2 = SO^4.C^5H^{11}.H + H^2O.$$

Now, on heating this mixture and passing a stream of ordinary alcohol through it, as above, ethamylic ether, or oxide of ethyl and amyl passes over first, then common ether, and ethyl-sulphuric acid remains behind in place of amyl-sulphuric acid:

$$\underbrace{SO^4.C^5H^{11}.H}_{\text{Amyl-sulphuric acid.}} + \underbrace{C^2H^5.H.O}_{\text{Alcohol.}} = \underbrace{C^2H^5.C^5H^{11}.O}_{\text{Oxide of ethyl and amyl.}} + \underbrace{SO^4H^2}_{\text{Sulphuric acid.}}$$

The sulphuric acid thus reproduced acts upon the ethyl-alcohol in the manner already described, the products being ethyl-sulphuric acid, ether, and water. The same products are obtained by distilling a mixture of ethyl-alcohol and amyl-alcohol with sulphuric acid.

The formation of ether from alcohol was formerly regarded as a simple process of dehydration. Ether being regarded as C^4H^5O and alcohol as its hydrate, $C^4H^5O.HO$, it was supposed that the sulphuric acid simply abstracted the water and left the ether. Against this view, however, it must be alleged that the quantity of water given off in the distillation is very nearly equal to the whole quantity supposed to be separated from the alcohol, which could not be the case if it were retained by the sulphuric acid. Moreover, the molecule of ether referred to the same vapour-volume as that of alcohol,

$C^4H^6O^2$, is not C^4H^5O, but $C^8H^{10}O^2$; or, according to the atomic weights adopted in this work, alcohol being C^2H^6O, ether is $C^4H^{10}O$. For these reasons, Mitscherlich, Berzelius, and other chemists have regarded the action of sulphuric acid upon alcohol as a *contact-action*, or *catalytic action*, a mode of expression which simply states the fact without explaining it.

Another objection to the views just mentioned, is that they take no account of the formation of ethyl-sulphuric acid. That this, however, is an essential step in the process of etherification is shown by the fact that, on distilling a mixture of alcohol and strong sulphuric acid, the quantity of ethyl-sulphuric acid constantly diminishes as the ether passes over, and that, if the acid be diluted so far as not to form ethyl-sulphuric acid, the mixture yields no ether by distillation. Liebig therefore supposed that the ethyl-sulphuric acid is resolved at a certain temperature (120° to 140° C.) into ether, sulphuric acid, and sulphuric anhydride:

$$2(C^2H^5.H.SO^4) = C^4H^{10}O + SO^4H^2 + SO^3$$

and that the sulphuric anhydride, uniting with water also present in the mixture, reproduces sulphuric acid. But ethyl-sulphuric acid when heated alone gives off, not ether but alcohol, even when heated to 140° or above in sealed tubes; but when heated with alcohol, it immediately yields ether. We are therefore led to regard the formation of ether as a result of the mutual decomposition of alcohol and ethyl-sulphuric acid, in the manner already explained.

When alcohol and strong sulphuric acid are heated together in sealed tubes, the alcohol being in excess, a layer of ether forms on the top of the liquid, but no ethyl-sulphuric acid is found in the lower stratum. If the sulphuric acid is in excess, no ether is formed (Graham, Chem. Soc. Qu. J. iii. 24). In the former case, it is probable that ethyl-sulphuric acid was first formed, and afterwards converted by the excess of alcohol into ether and sulphuric acid. Acid sulphate of potassium (Graham) and various other sulphates heated with alcohol in sealed tubes, also etherify it more or less completely, the sulphate being in some cases converted into a basic salt. The alums, namely common alum, ammonia-alum, potassio-ferric sulphate, and potassio-chromic sulphate heated with an equal weight of 98 per cent. alcohol, etherify it completely. In all these cases, the sulphate appears to give up a portion of its sulphuric acid, which then acts on the alcohol as above. (Reynoso, Ann. Ch. Phys. [3] xxviii. 385.)

Formation of Olefiant gas.—When 1 pt. of alcohol is heated with 3 or 4 pts. of strong sulphuric acid, the mixture begins, between 160° and 180° C., to blacken and thicken, swells up considerably and gives off olefiant gas C^2H^4, together with variable quantities of sulphurous anhydride, carbonic anhydride, carbonic oxide, oil of wine, acetic acid, acetic ether and formic acid, and a black residue is ultimately left consisting of a peculiar acid called thiomelanic acid and free sulphuric acid. By passing alcohol-vapour through a boiling mixture of 10 pts. of strong sulphuric acid and 3 pts. of water, olefiant gas and water are obtained, with scarcely any coloration of the mixture or formation of secondary products:

$$C^2H^6O = C^2H^4 + H^2O.$$

12. *Sulphuric anhydride*, SO^3, is dissolved by absolute alcohol, with evolution of heat, and forms neutral sulphate of ethyl $SO^4.(C^2H^5)^2$. When the vapour of the anhydride is passed into absolute alcohol, crystals of sulphate of carbyl, $C^2H^4.2SO^3$, are formed, together with ethionic, isethionic, ethyl-sulphuric and sulphuric acids.

13. *Phosphoric acid* mixed with alcohol at ordinary temperatures, converts part of it into ethyl-phosphoric acid. A mixture of phosphoric acid with a small quantity of alcohol yields olefiant gas but no ether; but if the alcohol is in excess, ether is first given off, then olefiant gas and a thick acid distillate probably consisting of neutral phosphate of ethyl, $PO^4.(C^2H^5)^3$. *Phosphoric anhydride* absorbs the vapour of anhydrous alcohol, forming ethyl-phosphoric acid $PO^4.C^2H^5.H^2$, and diethylphosphoric acid, $PO^4.(C^2H^5)^2.H$. *Arsenic acid* acts very much like phosphoric acid, producing ether and ethyl-arsenic acid. *Boric anhydride* (vitrefied boric acid) in the state of powder heated with absolute alcohol, gives off olefiant gas and leaves boric acid.

14. *Hydrochloric* acid gas is absorbed in large quantity by alcohol, and the solution when heated gives off chloride of ethyl. The same compound is obtained by distilling alcohol with strong hydrochloric acid, or with a mixture of common salt and sulphuric acid; but when a mixture of hydrochloric acid with a large excess of alcohol, either anhydrous or hydrated, is heated to 240° in a sealed tube, ether is formed as well as chloride of ethyl, these two liquids forming a layer on the surface, while the lower stratum consists chiefly of water and hydrochloric acid. The ether results from the action of alcohol on the chloride of ethyl already formed:

$$C^2H^5.Cl + C^2H^5.H.O = (C^2H^5)^2O + HCl.$$

The same transformation takes place, though slowly, even at 100° C. (A. Reynoso, Ann. Ch. Phys. [3] xlviii. 385.)

15. Many *metallic chlorides* act upon alcohol in a similar manner to hydrochloric acid, producing ether and chloride of ethyl. *Chloride of zinc* converts anhydrous alcohol into chloride of ethyl with a small quantity of ether. With hydrated alcohol, it yields at 155°C., ether and oil of wine, the quantity of which increases as the distillation goes on; hydrochloric acid is also given off, and basic chloride of zinc remains. When dichloride of tin is distilled with a considerable quantity of alcohol, ether and chloride of ethyl pass over between 140° and 170°, afterwards a compound of chloride of ethyl with dichloride of tin. (Kuhlmann, Ann. Ch. Pharm. xxxiii. 97, 192.)

Crystallised *protochloride of tin* distilled with alcohol yields ether, but no chloride of ethyl (Marchand); the same decomposition takes place in a sealed tube at 240°. Crystallised *chloride of manganese* and *protochloride of iron* also etherify alcohol completely when heated with it in sealed tubes to 240°; the chlorides of *cadmium, nickel, and cobalt* partially; in all these cases, the etherification takes place without blackening of the contents of the tube, and with little or no escape of gas when it is opened (Reynoso, Ann. Ch. Phys. [2] xlviii. 385). The formation of ether in these reactions may be explained by the following equations, given by Williamson for the case of chloride of zinc:

$$
\begin{aligned}
C^2H^5.H.O &+ ZnCl = C^2H^5.Zn.O + HCl.\\
C^2H^5.H.O &+ HCl = C^2H^5.Cl + H^2O.\\
C^2H^5.Cl &+ C^2H^5.Zn.O = (C^2H^5)^2O + ZnCl.
\end{aligned}
$$

With *sesquichloride of iron*, alcohol yields ether and chloride of ethyl between 130° and 140°C., afterwards hydrochloric acid and water, the residue consisting of sesquichloride of iron mixed with sesquioxide. With *chloride of aluminium*, chloride of ethyl is given off between 170° and 200°, afterwards hydrochloric acid, and alumina is left behind. *Trichloride* and *pentachloride of antimony* convert alcohol into chloride of ethyl, with a little ether, the residue consisting chiefly of oxychloride of antimony.

Protochloride of platinum boiled with alcohol of sp. gr. 0·813 to 0·893 is converted into a black explosive powder called *detonating platinum-deposit*, $C^2H^4Pt^2O$, the liquid acquiring a strong acid reaction and the odour of chloride of ethyl:

$$C^2H^6O + 2PtCl = C^2H^4Pt^2O + 2HCl.$$

The chloride of ethyl is formed by the action of the hydrochloric acid on another portion of the alcohol. (Zeise.)

A solution of 1 pt. of *dichloride of platinum* in 10 pts. of alcohol of sp. gr. 0·823, distilled to $\frac{1}{6}$, yields aldehyde, chloride of ethyl, and hydrochloric acid. The residual dark brown liquid deposits a considerable quantity of the black detonating powder just mentioned, and retains in solution the so-called *inflammable chloride of platinum*, $C^2H^4Pt^2Cl^2$, according to Zeise, or $C^2H^3Pt^2Cl^2$, according to Liebig. Its formation is represented by one of the following equations:

$$2C^2H^6O + 2PtCl^2 = C^2H^4Pt^2Cl^2 + \underbrace{C^2H^4O}_{\text{Aldehyde.}} + H^2O + 2HCl.\ \text{(Zeise.)}$$

$$3C^2H^6O + 4PtCl^2 = 2C^2H^3Pt^2Cl^2 + \underbrace{C^2H^4O}_{\text{Aldehyde.}} + 2H^2O + 4HCl.\ \text{(Liebig.)}$$

The formation of the black deposit is not an essential part of the reaction, and indeed takes place most abundantly when the dichloride of platinum contains protochloride.

Mercuric chloride, HgCl, dissolved in alcohol is slowly reduced to mercurous chloride Hg^2Cl. Potash added in excess to the alcoholic solution heated to 50°C., forms an amorphous yellow precipitate containing carbon, hydrogen, oxygen and mercury, the hydrogen being in smaller proportion than in alcohol. This precipitate heated to 200°, explodes without leaving any residue; heated in the moist state, it decomposes less violently, yielding mercury, water, and acetic acid (Sobrero and Selmi). Gerhardt and Werther did not succeed in preparing this compound.

16. *Trichloride of phosphorus* readily decomposes alcohol, forming chloride of ethyl, hydrochloric acid, tribasic phosphite of ethyl and phosphorous acid. (Béchamp Compt. rend. xl. 944.)

$$6(C^2H^5.H.O) + 2\,PCl^3 = 3C^2H^5Cl + 3\,HCl + PO^3.(C^2H^5)^3 + PO^3.H^3.$$

17. With *pentachloride* of phosphorus, the products are chloride of ethyl, hydrochloric and chlorophosphoric acid, PCl^3O:

$$C^2H^5.H.O + PCl^3.Cl^2 = C^2H^5Cl + HCl + PCl^3.O.$$

18. *Pentasulphide of phosphorus*, on the other hand, converts alcohol, not into two separate sulphides, but into the single compound *mercaptan*, or sulphide of ethyl and hydrogen:

$$5(C^2H^5.H.O) + P^2S^5 = 5(C^2H^5.H.S) + P^2O^5.$$

These last two reactions illustrate in a striking manner, the difference between monatomic and diatomic elements or radicles. In the former, the single atom of oxygen in alcohol is replaced by two atoms of chlorine, one of which unites with the ethyl, and the other with the hydrogen of the alcohol, forming two perfectly distinct chlorides; whereas in the latter, the oxygen of the alcohol is replaced by 1 atom of the diatomic element, sulphur, which being indivisible, binds together the ethyl and hydrogen into one single molecule of mercaptan. (Compare page 11.)

19. The *bromides* and *iodides* of phosphorus, hydrogen, and the metals, act like the chlorides. *Hydrofluoric* acid appears to convert alcohol into fluoride of ethyl.

20. *Potassium* and *sodium* rapidly decompose absolute alcohol, 1 atom of hydrogen being evolved and its place supplied by the metal; the resulting compound is an ethylate of potassium (C^2H^5KO) or ethylate of sodium, which crystallises from the saturated solution. The same compound appears to be formed by dissolving hydrate of potassium or sodium in absolute alcohol:

$$C^2H^5.H.O + KHO = C^2H^5.K.O + H^2O$$

The solution thus obtained exhibits in many cases the same reactions as that which is produced by dissolving the metal in alcohol.

21. Alcohol heated with *hydrate of potassium* (or sodium) yields hydrogen gas and an acetate:

$$C^2H^6O + KHO = C^2H^3KO^2 + 4H.$$

To produce this decomposition, a mixture of equal weights of the alkaline hydrate and pounded quick lime is moistened with alcohol, the excess of alcohol driven off at 100°, and the mixture gently heated without access of air. Hydrogen is then evolved, together with a small quantity of marsh gas, and the residue contains acetate of potassium, which, at a higher temperature, is resolved into marsh gas and carbonate of potassium (p. 17).

22. Alcohol-vapour passed over *anhydrous baryta* heated nearly to redness, yields olefiant gas, marsh gas and hydrogen, with a residue of carbonate of barium.

23. Gaseous *chloride of cyanogen* is readily absorbed by alcohol, but does not decompose it immediately. After a few days however, or more quickly if a little water is present or if the liquid is heated to 80°, chloride of ammonium separates out, while chloride of ethyl, carbamate of ethyl (urethane) and carbonate of ethyl remain in solution. The urethane and carbonate of ethyl are formed in the manner represented by the two following equations:

$$C^2H^6O + CNCl + H^2O = \underbrace{C^3H^7NO^2}_{\text{Urethane.}} + HCl$$

$$2C^2H^6O + CNCl + H^2O = \underbrace{CO^3(C^2H^5)^2}_{\text{Carbonate of ethyl.}} + NH^4Cl$$

The chloride of ethyl results from the action of the hydrochloric acid, produced as in the first equation, on the alcohol. (Wurtz. Ann. Ch. Pharm. lxxix. 77.)

24. Many *organic acids* when heated with alcohol convert it into compound ethers, with elimination of 1, 2, or 3 atoms of water, according as the acid is monobasic dibasic, or tribasic: *e. g.*

$$\underbrace{C^2H^5.H.O}_{\text{Alcohol.}} + \underbrace{C^2H^3O.H.O}_{\text{Acetic acid.}} = \underbrace{C^2H^3O.C^2H^5.O}_{\text{Acetic ether.}} + H^2O$$

$$2\underbrace{(C^2H^5.H.O)}_{\text{Alcohol.}} + \underbrace{CO^2.H^2.O^2}_{\text{Oxalic acid.}} = \underbrace{CO^2(C^2H^5)^2O^2}_{\text{Oxalic ether.}} + 2H^2O$$

$$3\underbrace{(C^2H^5.H.O)}_{\text{Alcohol.}} + \underbrace{C^6H^5O^4.H^3.O^3}_{\text{Citric acid.}} = \underbrace{C^6H^5O^4.(C^2H^5)^3.O^3}_{\text{Citric ether.}} + 3H^2O$$

With some acids, *e. g.* acetic and butyric acids, the transformation is easily effected; with others, as oxalic and hippuric acid, it takes a considerable time: in other cases again, as with benzoic acid, no ether is formed when the acid and the alcohol are merely distilled together; but on passing hydrochloric gas into the alcoholic solution of the acid, the ether is quickly formed. In this case, chloride of ethyl is first formed and afterwards decomposed by the organic acid. Other strong mineral acids, such as sulphuric acid, also facilitate the formation of these compound ethers.

Many polybasic organic acids form acid ethers when digested with alcohol; thus tartaric acid forms ethyl-tartaric acid $C^4H^4O^4(C^2H^5.H)O^2$.

The anhydrides of monobasic acids quickly convert alcohol into the corresponding ethers. (See *Dictionary of Arts, Manufactures, and Mines.*)

Compounds of Alcohol. Alcohol has a very strong affinity for *water*, and mixes with it in all proportions. The mixture is attended with slight evolution of heat, and also with contraction of volume, which gradually increases till the mixture contains 116 pts. water to 100 pts. alcohol. Strong alcohol absorbs moisture from the air. It abstracts water from the moist parts of the animal body, and coagulates them if they are of albuminous nature; hence its use in the preservation of anatomical preparations. From the same cause it destroys life in the veins.

Alcohol dissolves *iodine* and *bromine;* also *sulphur* and *phosphorus* in small quantities. *Gases* for the most part dissolve in alcohol more readily than in water. (See GASES, ABSORPTION OF.) Salts are, generally speaking, less soluble in alcohol than in water; indeed many salts quite insoluble in alcohol are easily soluble in water; *e. g.* the alkaline carbonates and sulphates. Chloride of mercury is, however, an exception to the general rule, being more soluble in alcohol than in water. Inorganic compounds, sparingly soluble in water, are, for the most part, quite insoluble in alcohol; so likewise are efflorescent compounds. But all deliquescent salts, excepting carbonate and phosphate of potassium and a few others, are soluble in alcohol.

Since alcohol does not dissolve all compounds which are soluble in water, it follows that many substances, when dissolved in alcohol, do not exhibit the same reactions towards other substances as when dissolved in water. Thus many acids, when dissolved in absolute alcohol do not redden litmus or decompose carbonate of barium or calcium, probably because the resulting calcium or barium salt would be insoluble in alcohol.

Alcohol readily dissolves *resins, ethers, essential oils, fats, alkaloids,* many *organic acids,* and in general, all substances containing a larger proportion of hydrogen.

ALCOHOLATES. Alcohol unites in definite proportion with several salts, forming crystallisable compounds, which however have but little stability and are almost all decomposed by water. These compounds were first obtained by Graham. (Graham, Phil. Mag. Ann. iv. 265. 331; Einbrodt, Ann. Ch. Pharm. lxv. 115; Chodnew, ibid. lxxi. 241; Lewy, Compt. rend. xxi. 371; Robiquet, J. Pharm. [3] xxvi. 161.)

Nitrate of magnesium dissolved in alcohol forms, on cooling from a boiling hot solution, a crystalline mass like margarin, containing $3C^2H^6O.NO^3Mg$.

Fused *chloride of calcium* dissolves in absolute alcohol, and the solution if surrounded with ice, deposits crystals containing $2C^2H^6O.CaCl$. This compound subjected to dry distillation yields nothing but carburetted hydrogen. If the alcohol contains a small quantity (about 1 per cent.) of water, the solution yields by evaporation sometimes a crystalline mass, sometimes a syrup, which dries up in vacuo to a white amorphous mass. Both the crystals and the syrup contain $2C^2H^6O.3CaCl + H^2O$.

Chloride of zinc forms with absolute alcohol a crystalline compound which contains $C^2H^6O.ZnCl$, and yields when heated, alcohol, chloride of ethyl, hydrochloric acid and oxide of zinc, but no ether.

Dichloride of tin and absolute alcohol, brought together in a vessel immersed in a freezing mixture, unite immediately, and on evaporating the solution in vacuo, over sulphuric acid and sticks of potash, crystals are formed containing $4C^2H^6O.Sn^2Cl^6O$. The crystals are very soluble in alcohol. They distil at 80° almost without decomposition (Lewy.) By cooling a mixture of 11·5 pts. of anhydrous alcohol, and 32·4 pts. of dichloride of tin in a frigorific mixture, Robiquet obtained a white powder which, when dissolved in alcohol, yielded by evaporation in vacuo over sulphuric acid, crystals containing $2C^2H^6O.SnCl^4$.

With *baryta,* alcohol forms the compound $2C^2H^6O.Ba^2O$, which is obtained by adding anhydrous baryta to absolute alcohol, filtering, and again adding baryta. If the alcoholic solution be then boiled, the compound separates in the form of a granular precipitate which redissolves on cooling. Water added to the solution throws down hydrate of barium. (Berthelot, Ann. Ch. Phys. [3] xlvi. 222.)

The following substances also form crystalline compounds with alcohol: sesquichloride of iron, protochloride of iron nitrate of calcium, and protochloride of manganese. (Graham.)

The alcohol in all these compounds may be regarded as analogous to water of crystallisation.

ALCOHOL-BASES. This name is frequently applied to the organic bases produced by the substitution of alcohol-radicles for the hydrogen in ammonia; such, as ethylamine, phenylamine, &c. (See AMINES.)

ALCOHOLOMETRY. (*Alcoométrie.*) The value of spirituous liquors depends upon the quantity of alcohol which they contain. This may be determined in various ways: viz. by the specific gravity of the mixture, by its boiling-point, by the tension of its vapour, by its rate of expansion, and by estimating the proportion of carbon contained in it by combustion with oxide of copper. But of all these methods, that which depends upon the density is almost always employed for practical purposes, other methods being resorted to only when the mixture of alcohol and water is associated with foreign substances, such as sugar, or colouring matter, or salts, in sufficient quantity to produce a material alteration of the density.

To determine the amount of alcohol in a spirituous liquor by its density, it is necessary to know beforehand the density corresponding to each particular proportion of alcohol and water. If these liquids were capable of mixing without alteration of volume, the specific gravity of each particular mixture might be calculated from the proportions of alcohol and water contained in it, and the known specific gravity of absolute alcohol. This however is not the case, the combination of alcohol and water being attended with a contraction of volume varying in amount with the temperature. For this reason the specific gravity of each mixture of alcohol and water must be determined by direct experiment, and the results collected in tables.

The importance of this object for the purposes of revenue induced the British government to employ Sir Charles Blagden to institute a very extensive and accurate series of experiments on the density of spirit of various degrees of strength. The determinations, which were made by Gilpin under Blagden's direction, were first published in 1790, afterwards twice repeated to obtain greater accuracy, and published in the Philosophical Transactions for 1794.

The specific gravity of the mixtures of alcohol and water was determined by accurately weighing a quantity of the liquid in a flask having a long narrow neck, and filled with it up to a certain mark, the weight of an equal quantity of distilled water having been previously ascertained. In this manner, the specific gravity of 40 mixtures was determined, each at 15 different temperatures. The standard alcohol used to mix with the water was not absolute, but had a specific gravity of 0·82514; for convenience, however, it was supposed to be = 0·825, a corresponding deduction being made from all the numbers in the table.

TABLE I.—*Showing the Specific Gravity of various mixtures of Alcohol (of Specific Gravity* 82500 *at* 60° *Fahr.) and Water at different Temperatures, the Specific Gravity of water at* 60° *Fahr. being* 100000.

Heat.	The pure spirit.	100 grains of spirit to 5 gr. of water.	100 grains of spirit to 10 gr. of water.	100 grains of spirit to 15 gr. of water.	100 grains of spirit to 20 gr. of water.	100 grains of spirit to 25 gr. of water.	100 grains of spirit to 30 gr. of water.	100 grains of spirit to 35 gr. of water.	100 grains of spirit to 40 gr. of water.	100 grains of spirit to 45 gr. of water.	100 grains of spirit to 50 gr. of water.
30 F.	·83896	·84995	·85957	·86825	·87585	·88282	·88921	·89511	·90054	90558	·91023
35	83672	84769	85729	86587	87357	88059	88701	89294	89839	90345	90811
40	83445	84539	85507	86361	87184	87838	88481	89073	89617	90127	90596
45	83214	84310	85277	86131	86905	87613	88255	88849	89396	89909	90380
50	82977	84076	85042	85902	86676	87384	88030	88626	89174	89684	90160
55	82736	83834	84802	85664	86441	87150	87796	88393	88945	89458	89933
60	82500	83599	84568	85430	86208	86918	87569	88169	88720	89232	89707
65	82262	83362	84334	85193	85976	86686	87337	87938	88490	89006	89479
70	82023	83124	84092	84951	85736	86451	87105	87705	88254	88773	89252
75	81780	82878	83851	84710	85496	86212	86864	87466	88018	88538	89018
80	81530	82631	83603	84467	85248	85966	86622	87228	87776	88301	88781
85	81291	82396	83371	84243	85036	85757	86411	87021	87590	88120	88609
90	81044	82150	83126	84001	84797	85518	86172	86787	87360	87889	88376
95	80794	81900	82877	83753	84550	85272	85928	86542	87114	87654	88146
100	80548	81657	82639	83513	84038	85031	85688	86302	86879	87421	87915

TABLE I. (*continued*).

Heat	100 grains of spirit to 55 gr. of water.	100 grains of spirit to 60 gr. of water.	100 grains of spirit to 65 gr. of water.	100 grains of spirit to 70 gr. of water.	100 grains of spirit to 75 gr. of water.	100 grains of spirit to 80 gr. of water.	100 grains of spirit to 85 gr. of water.	100 grains of spirit to 90 gr. of water.	100 grains of spirit to 95 gr. of water.	100 grains of spirit to 100 gr. of water.
30° F.	·91449	·91847	·92217	·92563	·92889	·93191	·93474	·93741	·93991	·94222
35	91241	91640	92009	92355	92680	92986	93274	93541	93790	94025
40	91026	91428	91799	92151	92476	92783	93072	93341	93592	93827
45	90812	91211	91584	91937	92264	92570	92859	93131	93382	93621
50	90596	90997	91370	91723	92051	92358	92647	92919	93177	93419
55	90367	90768	91144	91502	91837	92145	92436	92707	92963	93208
60	90144	90549	90927	91287	91622	91933	92225	92499	92758	93002
65	89920	90328	90707	91066	91400	91715	92010	92283	92546	92794
70	89695	90104	90484	90847	91181	91493	91793	92069	92333	92580
75	89464	89872	90252	90617	90952	91270	91569	91849	92111	92364
80	89225	89639	90021	90385	90723	91046	91340	91622	91891	92142
85	89043	89460	89843	90209	90558	90882	91186	91465	91729	91969
90	88817	89230	89617	89988	90342	90668	90967	91248	91511	91751
95	88588	89003	89390	89763	90119	90443	90747	91029	91290	91531
100	88357	88769	89158	89536	89889	90215	90522	90805	91066	91310

Heat.	95 grains of spirit to 100 gr. of water.	90 grains of spirit to 100 gr. of water.	85 grains of spirit to 100 gr. of water.	80 grains of spirit to 100 gr. of water.	75 grains of spirit to 100 gr. of water.	70 grains of spirit to 100 gr. of water.	65 grains of spirit to 100 gr. of water.	60 grains of spirit to 100 gr. of water.	55 grains of spirit to 100 gr. of water.	50 grains of spirit to 100 gr. of water.
30° F.	·94447	·94675	·94920	·95173	·95429	·95681	·95944	·96209	·96470	·96719
35	94249	94484	94734	94988	95246	95502	95772	96048	96315	96579
40	94058	94295	94547	94802	95060	95328	95602	95879	96159	96434
45	93860	94096	94348	94605	94871	95143	95423	95703	95993	96280
50	93658	93897	94149	94414	94683	94958	95243	95534	95831	96126
55	93452	93696	93948	94213	94486	94767	95057	95357	95662	95966
60	93247	93493	93749	94018	94296	94579	94876	95181	95493	95804
65	93040	93285	93546	93822	94099	94388	94689	95000	95318	95635
70	92829	93076	93337	93616	93898	94193	94500	94813	95139	95469
75	92613	92865	93132	93413	93695	93989	94301	94623	94957	95292
80	92393	92646	92917	93201	93488	93785	94102	94431	94768	95111

Heat.	45 grains of spirit to 100 gr. of water.	40 grains of spirit to 100 gr. of water.	35 grains of spirit to 100 gr. of water.	30 grains of spirit to 100 gr. of water.	25 grains of spirit to 100 gr. of water.	20 grains of spirit to 100 gr. of water.	15 grains of spirit to 100 gr. of water.	10 grains of spirit to 100 gr. of water.	5 grains of spirit to 100 gr. of water.
30° F.	·96967	·97200	·97418	·97635	·97860	98108	·98412	·98814	·99334
35	96840	97086	97319	97556	97801	98076	98397	98804	99344
40	96706	96967	97220	97472	97737	98033	98373	98795	99345
45	96563	96840	97110	97384	97666	97980	98338	98774	99338
50	96420	96708	96995	97284	97589	97920	98293	98745	99316
55	96272	96575	96877	97181	97500	97847	98239	98702	99284
60	96122	96437	96752	97074	97410	97771	98176	98654	99244
65	95962	96288	96620	96959	97309	97688	98106	98594	99194
70	95802	96143	96484	96836	97203	97596	98028	98527	99134
75	95638	95987	96344	96708	97086	97495	97943	98454	99066
80	95467	95826	96192	96568	96963	97385	97845	98367	98991

Gilpin's tables do not give directly the quantity of absolute alcohol contained in spirit of any given density. In this respect, however, they have been completed by the experiments of Tralles, who in 1811 (Gilbert's Annalen, xxxviii. 386), determined the specific gravity of alcohol, dehydrated as completely as possible by means of chloride of calcium, and likewise the strength of Gilpin's standard spirit, having a specific gravity of 0·825 at 60° F. He found that the specific gravity of absolute alcohol at 60° F. compared with that of water at its maximum density is 0·7939 (or 0·7946 compared with water at 60°) and that Gilpin's standard spirit contains in 100 parts by weight, 89·2 parts of anhydrous alcohol, and 10·8 parts of water. Proceeding upon these data, Tralles calculated the proportions of absolute alcohol and water contained in spirit of various densities; the results are given in Table II. p. 83.

The proportions of alcohol in spirit of wine may be expressed either by weight or by volume. The former mode of expression is by far the simpler and more definite, because the proportion by weight is independent of the temperature, whereas the proportion by volume varies with the temperature, being affected by the different rates of expansion of alcohol and water. For scientific purposes, therefore, the strength of spirit is always expressed in percentage by weight. In commerce, on the contrary, the method by volume is always adopted, spirit being generally bought and sold by measure, not by weight. It becomes therefore necessary to know how to calculate the composition by volume from the composition by weight and the observed specific gravity.

Let S be the specific gravity of the spirit (mixture of alcohol and water): a the quantity of alcohol in 100 parts by weight, and therefore $100 - a$ the quantity of water; V the volume of the spirit referred to a unit of volume, such that a quantity of water which fills it is the unit of weight (*e. g.* if the weight is expressed in grammes, V is measured in cubic centimetres) then:

$$100 = V \,.\, S$$

If then, the specific gravity of anhydrous alcohol at the observed temperature compared with water at the same temperature be s, the volumes of alcohol and water contained in the spirit are:

$$\frac{a}{s} \quad \text{and} \quad 100 - a$$

and consequently, the proportions of alcohol and water in 100 volumes of the spirit are:

$$\frac{a}{s} \cdot \frac{100}{V} = a . \frac{S}{s} \text{ volumes of alcohol.}$$

$$\text{and: } (100 - a) \cdot \frac{100}{V} = (100 - a)\, S \text{ volumes of water.}$$

For example: from the table p. 85 it appears that spirit containing 77·09 per cent. of alcohol by weight has at 60° F. a sp. gr. of 0·8555, referred to water at the same temperature, and the specific gravity of absolute alcohol referred to the same standard is 0·7946: hence the percentage of alcohol by volume is:

$$77{\cdot}09 \cdot \frac{8555}{7946} = 83{\cdot}00$$

and the percentage by volume of water is:

$$(100 - 77{\cdot}09) \,.\, 0{\cdot}8555 = 22{\cdot}91 \,.\, 0{\cdot}8555 = 20{\cdot}60$$

the whole being measured at 60° F.

The volumes of alcohol and water thus obtained amount together to more than 100, in the preceding example to 103·60; and accordingly, if 83·00 measures of alcohol be mixed with 20·60 measures of water, both at 60° F., the mixture, after it has cooled to 60° F., will fill exactly 100 measures, and the spirit thus produced will contain 83 volumes per cent. of alcohol. (Respecting the contraction which takes place on mixing alcohol and water in various proportions, see Rudberg, Pogg. Ann. xiii. 196; also Kopp, ibid. liii. 356.)

When the volume per cent. in a mixture of alcohol and water is given, the weight per cent. is found from the equation:

$$a = V \cdot \frac{s}{S}$$

Thus, according to the table (p. 85) spirit containing 68 volumes per cent. of alcohol has a sp. gr. of 0·8949 at 60° F. Hence the weight per cent. of alcohol is:

$$a = 68 \,.\, \frac{7946}{8949} = 60{\cdot}38$$

that is to say: 100 lbs. of this spirit contain 69·38 lbs. of alcohol and 39·62 lbs. of water.

The specific gravity of aqueous alcohol may be determined by any of the ordinary methods; either by weighing in a specific gravity bottle, or by means of the hydrometer (See SPECIFIC GRAVITY and HYDROMETER) and thence the percentage of anhydrous alcohol by weight and by volume may be determined by means of the preceding formulæ and the tables to be given hereafter. To facilitate these determinations, hydrometers are constructed with scales marking directly the percentage of alcohol by volume, and sometimes also by weight, of the spirit in which they are immersed. Such instruments are called ALCOHOLOMETERS. Three of them are in use, viz. the alcoholometer of Tralles, which gives the percentage volume for the temperature of 60° F. = $12\frac{4}{9}$ R. = $15\frac{5}{9}$ C.; Gay-Lussac's alcoholometer, which likewise indicates percentage by volume at 15° C.; and Meissner's, which gives percentages both by weight and volume, the latter for the temperature of 14° R = 17·5° C.

As the scales of these instruments are constructed for different temperatures, they cannot be expected to agree exactly; but the differences arising from this cause are trifling. Greater discrepancies however arise from the different experimental data upon which the scales have been constructed; that of Tralles being founded on the exact and extensive observations of Gilpin, and Meissner's on experiments of his own. Gay-Lussac has not stated on what experimental data his observations are founded, but his numbers agree very nearly with those of Tralles, the differences never exceeding ⅓ per cent. for the same specific gravity.

The following table gives the percentages of anhydrous alcohol both by weight and volume of mixtures of alcohol and water, according to their specific gravity as determined by Tralles from the observations of Gilpin; also the specific gravities as determined by Gay-Lussac. They are deduced from Tralles' numbers by multiplying by 1·0009. The corresponding indications of the hydrometers of Beck, Baumé, and Cartier, are likewise added.

TABLE II.

Volumes per cent. according to Tralles.	Weights per cent.	Specific gravities according to Gilpin at 60° F.=$15\frac{5}{9}$ C.	Specific gravities according to Gay-Lussac at 15° C.	Degrees of Beck's Hydrometer.	Degrees of Baumé's Hydrometer.	Degrees of Cartier's Hydrometer.
0	0	1·0000	1·0000	0·0	10	11
1	0·80	0·9985	—	—	—	—
2	1·60	9970	—	—	—	—
3	2·40	9956	—	—	—	—
4	3·20	9942	—	1·0	—	—
5	4·00	9928	—	1·2	11	12
6	4·81	9915	—	1·4	—	—
7	5·62	9902	—	1·6	—	—
8	6·43	9890	—	1·9	—	—
9	7·24	9878	—	2·1	—	—
10	8·05	9866	—	2·3	12	—
11	8·87	9854	—	2·5	—	—
12	9·69	9844	—	2·7	—	13
13	10·51	9832	—	2·9	—	—
14	11·33	9821	—	3·1	—	—
15	12·15	9811	—	3·3	—	—
16	12·98	9800	—	3·5	13	—
17	13·80	9790	—	3·6	—	—
18	14·63	9780	—	3·8	—	—
19	15·46	9770	—	4·0	—	14
20	16·28	9760	—	4·2	—	—
21	17·11	9750	—	4·4	—	—
22	17·95	9740	—	4·6	—	—
23	18·78	9729	—	4·8	14	—
24	19·62	9719	—	4·9	—	—
25	20·46	9709	—	5·1	—	—
26	21·30	9698	—	5·3	—	15
27	22·14	9688	—	5·5	—	—
28	22·99	9677	—	5·7	—	—
29	23·84	9666	—	5·9	15	—
30	24·69	9655	0·9656	6·1	—	—
31	25·55	9643	—	6·4	—	—
32	26·41	9631	—	6·6	—	—

TABLE II. (*continued*).

Volumes per cent. according to Tralles.	Weights per cent.	Specific Gravities according to Gilpin at 60° F.=$15\frac{5}{9}$C.	Specific Gravities according to Gay-Lussac at 15° C.	Degrees of Beck's Hydrometer.	Degrees of Cartier's Hydrometer.	Degrees of Baumé's Hydrometer.
33	27·27	0·9618	0·9656	6·8	15	16
34	28·13	9605	—	7·0	16	—
35	28·99	9592	9595	7·2	—	—
36	29·86	9579	—	7·5	—	—
37	30·74	9565	—	7·7	—	—
38	31·62	9550	—	8·0	—	17
39	32·50	9535	—	8·3	17	—
40	33·39	9519	9523	8·6	—	—
41	34·28	9503	—	8·0	—	—
42	35·18	9487	—	9·2	—	18
43	36·08	9470	—	9·5	18	—
44	36·99	9452	—	9·8	—	—
45	37·90	9435	9440	10·2	—	—
46	38·82	9417	—	10·5	19	19
47	39·75	9399	—	10·9	—	—
48	40·66	9381	—	11·2	—	—
49	41·59	9362	—	11·6	—	—
50	42·52	9343	9348	11·9	20	20
51	43·47	9323	—	12·3	—	—
52	44·42	9303	—	12·7	—	—
53	45·36	9283	—	13·1	21	—
54	46·32	9262	—	13·5	—	21
55	47·29	9242	9248	13·9	—	—
56	48·26	9221	—	14·3	22	—
57	49·23	9200	—	14·8	—	22
58	50·21	9178	—	15·2	23	—
59	51·20	9156	—	15·6	—	—
60	52·20	9134	9141	16·1	—	23
61	53·20	9112	—	16·5	24	—
62	54·21	9090	—	17·0	—	—
63	55·21	9067	—	17·5	25	24
64	56·22	9044	—	18·0	—	—
65	57·24	9021	9027	18·4	—	25
66	59·27	8997	—	18·9	26	—
67	59·32	8973	—	19·4	—	—
68	60·38	8949	—	20·0	27	26
69	61·42	8925	—	20·5	—	—
70	62·50	8900	8907	21·0	28	27
71	63·58	8875	—	21·5	—	—
72	64·66	8850	—	22·1	—	—
73	65·74	8824	—	22·6	29	28
74	66·83	8799	—	23·2	—	—
75	67·93	8773	8799	23·8	30	29
76	69·05	8747	—	24·4	—	—
77	70·18	8720	—	25·0	31	30
78	71·31	8693	—	25·6	—	—
79	72·45	8664	—	26·2	32	—
80	73·59	8639	8645	26·8	—	31
81	74·74	8611	—	27·4	33	—
82	75·91	8583	—	28·0	34	32
83	77·09	8555	—	28·7	—	—
84	78·29	8526	—	29·4	35	33
85	79·50	8496	8502	30·1	—	—
86	80·71	8466	—	30·8	36	34

TABLE II. (*continued*).

Volumes per cent. according to Tralles.	Weights per cent.	Specific Gravities according to Gilpin at 60° = $15\frac{5}{9}$° C.	Specific Gravities according to Gay-Lussac at 15° C.	Degrees of Beck's Hydrometer	Degrees of Baumé's Hydrometer.	Degrees of Cartier's Hydrometer.
87	81·94	0·8436	0·8502	31·5	37	35
88	83·19	8405	—	32·2	—	—
89	84·46	8373	—	33·0	38	36
90	85·75	8340	8346	33·8	—	—
91	87·09	8306	—	34·7	39	37
92	88·37	8272	—	35·5	40	38
93	89·71	8237	—	36·4	41	—
94	91·07	8201	—	37·3	—	39
95	92·46	8164	8168	38·2	42	40
96	93·89	8125	—	39·2	43	—
97	95·34	8084	—	40·3	44	41
98	96·84	8041	—	41·5	45	42
99	98·39	7995	—	42·7	46	43
100	100·00	7946	7947	43·9	47	—

The use of this table may be extended to intermediate numbers by interpolation. Thus, if it be required to find the composition by volume of a mixture of 50 lbs. of anhydrous alcohol and 50 lbs. of water, we find from the table that:

49·23 p. c. by weight corresponds to 57 p. c. by volume
and: 50· 2 „ „ 58 „
difference 0·98 and 1

Hence, to find the fraction which must be added to the number 57 to give the percentage required, we have the proportion:

$$0{\cdot}98 \ : \ (50 - 49{\cdot}23) = 1 \ : \ x$$

which gives: $$x = \frac{77}{98} = 0{\cdot}8$$

Whence it appears that 100 volumes (measured at 60° F.) of a spirit containing equal weights of alcohol and water contain 57·8 volumes of alcohol, also at 60°.

Again, let it be required to find the composition of a spirit having at 60° Fahr. the specific gravity 0·8955, compared with water at the same temperature; this number is intermediate between the numbers 8949 and 8973 in the third column of the table, which correspond to the volume per centages 67 and 68; hence the proportion:

$$8973 - 8949 \ : \ 8973 - 8955 = 1 \ : \ x$$

which gives $$x = \frac{18}{24} = \tfrac{3}{4}$$

that is to say, 100 measures of spirit of sp. 0·8955 at 60° Fahr. contain $67\frac{3}{4}$ measures of anhydrous alcohol.

Meissner's results are given in his "Aräometrie in ihrer Anwendung auf Chemie und Technik," Wien, 1816. Th. ii. 27. They differ somewhat from the preceding.

TABLE II. *a.—Specific Gravity* (*according to Meissner*) *of Hydrated Alcohol containing in* 100 *parts:*

Alcohol.	By Weight.		By Volume.	
Parts.	At 20° C.	At 17·5° C.	At 20° C.	At 17·5° C.
100	0·791	0·793	0·791	0·793
95	0·805	0·801	0·809	0·811
90	0·818	0·822	0·824	0·828
85	0·831	0·835	0·839	0·843
80	0·843	0·847	0·854	0·857
75	0·856	0·859	0·867	0·869
70	0·868	0·870	0·880	0·883

TABLE II. *a.* (*continued*).

Alcohol.	By Weight.		By Volume.	
Parts.	At 20° C.	At 17·5° C.	At 20° C.	At 17·5° C.
65	0·880	0·883	0·893	0·896
60	0·892	0·895	0·906	0·907
55	0·904	0·906	0·917	0·919
50	0·915	0·917	0·928	0·930
45	0·926	0·928	0·938	0·940
40	0·937	0·939	0·947	0·949
35	0·947	0·948	0·955	0·958
30	0·955	0·958	0·963	0·964
25	0·963	0·965	0·969	0·970
20	0·970	0·971	0·975	0·976
15	0·977	0·977	0·981	0·980
10	0·984	0·983	0·987	0·986
5	0·992	0·991	0·993	0·993
0	1·000	1·000	1·000	1·000

TABLE II. *b.—The following Table is given by Fownes* (Manual of Chemistry, 3rd Ed. p. 591), *the Specific Gravities being taken at* 15·6° C. *or* 60 Fahr.

Percentage by weight.	Specific Gravity.	Percentage by weight.	Specific Gravity.	Percentage by weight.	Specific Gravity.
0·5	0·9991	34	0·9511	68	0·8769
1	0·9981	35	0·9490	69	0·8745
2	0·9965	36	0·9470	70	0·8721
3	0·9947	37	0·9452	71	0·8696
4	0·9930	38	0·9434	72	0·8672
5	0·9914	39	0·9416	73	0·8649
6	0·9898	40	0·9396	74	0·8625
7	0·9884	41	0·9376	75	0·8603
8	0·9869	42	0·9356	76	0·8581
9	0·9855	43	0·9335	77	0·8557
10	0·9841	44	0·9314	78	0·8533
11	0·9828	45	0·9292	79	0·8508
12	0·9815	46	0·9270	80	0·8483
13	0·9802	47	0·9249	81	0·8459
14	0·9789	48	0·9228	82	0·8434
15	0·9778	49	0·9206	83	0·8408
16	0·9766	50	0·9184	84	0·8382
17	0·9753	51	0·9160	85	0·8357
18	0·9741	52	0·9135	86	0·8331
19	0·9728	53	0·9113	87	0·8305
20	0·9716	54	0·9090	88	0·8279
21	0·9704	55	0·9069	89	0·8254
22	0·9691	56	0·9047	90	0·8228
23	0·9678	57	0·9025	91	0·8199
24	0·9665	58	0·9001	92	0·8172
25	0·9652	59	0·8979	93	0·8145
26	0·9638	60	0·8956	94	0·8118
27	0·9623	61	0·8932	95	0·8089
28	0·9609	62	0·8908	96	0·8061
29	0·9593	63	0·8886	97	0·8031
30	0·9578	64	0·8863	98	0·8001
31	0·9560	65	0·8840	99	0·7969
32	0·9544	66	0·8816	100	0·7938
33	0·9528	67	0·8793		

It is often necessary to take the specific gravity of spirit at a temperature different from the standard. In that case, the percentage of alcohol may be determined by means of the two following tables, given by Tralles.

TABLE III. — *Specific Gravity of Spirit of different strengths at Temperatures from 30° Fahr. to 100° Fahr. that of Water at 39·83 Fahr. being* = 10000.

Quantity of Alcohol at 60° Fahr. in percentages by Volume.	Temperatures (Fahr.)														
	30°.	35°.	40°.	45°.	50°.	55°.	60°.	65°.	70°.	75°.	80°.	85°.	90°.	95°.	100°.
0	9998	10000	10000	10000	9998	9995	9991	9986	9980	9974	9967	9959	9951	9941	9931
5	9928	9929	9929	9928	9926	9923	9919	9914	9908	9901	9894	9816	9877	9868	9857
10	9872	9672	9871	9869	9866	9862	9857	9851	9844	9837	9828	9820	9810	9800	9789
15	9827	9825	9823	9819	9814	9808	9802	9795	9787	9777	9768	9758	9747	9735	9723
20	9790	9786	9780	9774	9767	9759	9751	9742	9732	9721	9710	9698	9685	9672	9658
25	9756	9748	9739	9731	9721	9710	9700	9689	9676	9664	9650	9637	9622	9607	9591
30	9719	9708	9697	9685	9672	9659	9646	9632	9618	9603	9587	9571	9555	9538	9521
35	9672	9658	9644	9629	9614	9599	9583	9566	9550	9533	9515	9497	9479	9461	9442
40	9613	9597	9580	9562	9545	9528	9510	9492	9473	9454	9435	9416	9396	9376	9356
45	9539	9521	9503	9484	9466	9416	9427	9407	9387	9367	9347	9326	9305	9284	9263
50	9453	9454	9415	9395	9375	9355	9335	9314	9293	9272	9251	9229	9207	9185	9162
55	9358	9338	9318	9297	9276	9255	9234	9212	9191	9169	9147	9125	9102	9079	9056
60	9253	9233	9212	9191	9169	9148	9126	9104	9082	9059	9036	9013	8990	8967	8943
65	9143	9122	9101	9080	9058	9035	9013	8991	8968	8945	8921	8898	8875	8851	8826
70	9025	9004	8982	8960	8937	8914	8892	8869	8846	8823	8799	8775	8751	8727	8702
75	8900	8878	8856	8833	8811	8788	8765	8742	8719	8695	8671	8646	8622	8598	8573
80	8768	8746	8723	8701	8678	8654	8631	8608	8584	8560	8535	8511	8487	8462	8437
85	8627	8604	8581	8558	8535	8511	8488	8464	8440	8416	8392	8367	8343	8318	8293
90	8472	8449	8426	8426	8380	8356	8332	8308	8284	8260	8235	8211	8186	8161	8136

TABLE IV.—*Volumes of Alcohol of Specific Gravity* 7939 *at* 60° *Fahr. which would be contained at* 60° *Fahr. in* 100 *measures of Spirit exhibiting at the several Temperatures (Fahr.) stated at the heads of the columns the following apparent Specific Gravities as determined with a Glass vessel or instrument.*

Volumes of Alcohol.	30°.	35°.	40°.	45°.	50°.	55°.	60°.	65°.	70°.	75°.	80°.	85°.
0	9994	9997	9997	9998	9997	9994	9991	9987	9981	9976	9970	9962
5	9924	9926	9929	9926	9925	9922	9919	9915	9909	9903	9897	9889
10	9868	9869	9868	9867	9865	9861	9857	9852	9845	9839	9831	9823
15	9823	9822	9820	9817	9813	9807	9802	9796	9788	9779	9771	9761
20	9786	9782	9777	9772	9766	9759	9751	9743	9735	9723	9713	9701
25	9752	9745	9737	9729	9720	9709	9700	9690	9678	9666	9653	9640
30	9715	9705	9694	9683	9671	9658	9546	9633	9619	9605	9590	9574
35	9668	9655	9641	9627	3612	9598	9583	9567	9551	9535	9518	9500
40	9609	9594	9577	9560	9544	9527	9510	9493	9474	9456	9438	9419
45	9535	9518	9500	9482	9464	9445	9427	9408	9388	9369	9350	9329
50	9449	9431	9413	9393	9374	9354	9335	9315	9294	9274	9253	9232
55	9354	9335	9316	9295	9275	9254	9234	9213	9192	9171	9150	9128
60	9249	9230	9210	9189	9168	9147	9126	9105	9083	9061	9039	9016
65	9140	9120	9099	9078	9056	9034	9013	8992	8969	8947	8924	8001
70	9021	9001	8980	8958	8936	8913	8892	8870	8847	8825	8801	8778
75	8896	8875	8854	8832	8810	8787	8765	8742	8720	8697	8673	8619
80	8764	8743	8721	8699	8676	8653	8631	8609	8585	8562	8538	8514
85	8623	8601	8579	8556	8533	8510	8488	8465	8441	8468	8394	8370
90	8469	8446	8423	8401	8379	8355	8332	8309	8285	8262	8238	8214

REDUCTIONS FOR A *Brass* INSTRUMENT.

To be deducted from the Specific Gravities.						To be added to the Specific Gravities.					
−5	−4	−3	−2	−2	−1	0	+1	+2	+2	+3	+4

In Table III. the specific gravity of the spirit is supposed to be compared with that of water at the maximum density, and to be corrected for the expansion of the vessel or instrument with which the determination is made. These densities may be reduced to those compared with water at 60° F. (as in Table II.), by multiplying them all by 1·0009.

To find by means of this table the strength of a spirit, when either the specific gravity or the temperature is not given exactly as in the tables, we proceed by interpolation as in the calculations connected with Table II. (p. 85.) But if neither temperature nor specific gravity is exactly given in the table, the calculation is made as in the following example. Let it be required to find the strength of a spirit of sp. gr. 0·9321 at 77° F.

Per cent. of Alcohol.	Specific Gravity at 75° F.	Specific Gravity at 80° F.	Difference.
45	9367	9347	20
50	9272	9251	21
Difference 5	95	96	

Hence the sp. gr. for 77° F., and for:

$$45 \text{ p. c. alcohol is } 9367 - 2 \times \frac{20}{5} = 9359$$

$$50 \quad ,, \quad 9272 - 2 \times \frac{21}{5} = 9263·6$$

$$\text{Difference} = 95·4$$

Calling this difference 95, it follows that to each 1 per cent. of alcohol there corresponds at 77° F. a difference of 19 in the specific gravity, and consequently the volume per cent. of alcohol corresponding to the specific gravity 9321 is

$$45 + \frac{9359 - 9321}{19} = 45 + \frac{38}{19} = 47 \text{ vol. p. c.}$$

This result shows that the spirit in question, when cooled down to the normal temperature of 60° F. contains in 100 measures, 47 measures of absolute alcohol; this is not, however, the actual proportion by volume at 77°, because alcohol and water expand at different rates.

Table IV. exhibits in the same manner as Table III. the strength of spirit according to its specific gravity, but on the supposition that the specific gravity is determined with a glass instrument, and is not corrected for the expansion of the glass: hence the expression "apparent specific gravity."

If the specific gravity of a sample of spirit has been determined at one temperature and its volume measured at another, the amount of alcohol in it may be calculated as in the following example: 350 quarts of spirit are measured out at 75° F., and the specific gravity determined with a glass instrument at 65° F. is 0·8609. By Table IV. the strength of this spirit is 80 per cent., that is to say, 100 volumes of it measured at 60° F. contain 80 vol. of alcohol. By Table III. the specific gravities of spirit of 80° per cent. for the temperatures 60° and 75° are 8631 and 8560. Consequently the volumes of a given weight of the spirit at 60° and 75° are as 8560 : 8631, and therefore the 350 quarts of spirit would, if cooled to 60°, measure $350 \times \frac{8560}{8631} = 347·12$ quarts; and this volume of liquid at the strength of 80 per cent. contains 277·7 quarts of real alcohol.

To ensure perfect accuracy, the expansion of the vessel in which the spirit is measured ought to be taken into account; but for commercial purposes, to which calculations of this kind chiefly apply, this correction is too small to be of any importance.

The quantity of alcohol of 60° F. in 100 volumes of spirit of the same temperature is called the *strength* (*Stärke; force*), of the spirit; and the quantity of alcohol of 60° F. in 100 volumes of spirit of any given temperature is called the *real amount of alcohol* (*wahrer Alkoholgehalt; Richesse*). Thus in the example just given, the strength of the spirit is 80. but the real amount of alcohol is $\frac{277·7}{350} \times 100 = 79·3$.

The following Tables, V. and VI., exhibit the *strength* and the *real amount of alcohol* of a sample of spirit, according to the indications of the alcoholometer and the thermometer. If, for example, the alcoholometer marks 75 per cent. in a spirit whose temperature is 50° F., we find from line 16, column 6, of Table V. that the strength of the spirit is 76·7, and from the corresponding place in Table VI. that its real amount of alcohol is 77·1 per cent.

Table V.—*Showing the Amount of Alcohol which a given sample of Spirit would contain at 60° F. according to the indication of a glass Alcoholometer, immersed in it at any other temperature.*

Indications of the Alcoholometer.	Strength of the Spirit, when tested by the Alcoholometer at the following temperatures.											
	0° 0 32	2° 2·5 36·5	4° 5 41	6° 7·5 45·5	8° 10 50	10° 12·5 54·5	12° 15 59	14° 17·5 63·5	16° 20 68	18° 22·5 72·5	20° 25 77	22° 27·5 81·5	24 R 30 C 86 F.
0	0·3	0·4	0·4	0·4	0·4	0·2	0	—	—	—	—	—	—
5	5·4	5·5	5·5	5·5	5·4	5·2	5·0	4·7	4·4	4·1	3·7	3·2	2·5
10	11·2	11·1	11·0	10·9	10·7	10·4	10·1	9·7	9·2	8·8	8·3	7·8	7·3
15	17·8	17·4	17·0	16·5	16·0	15·6	15·1	14·6	14·0	13·4	12·8	12·2	11·6
20	24·7	23·9	23·1	22·3	21·7	20·9	20·2	19·5	18·8	18·0	17·2	16·5	15·7
25	31·2	30·1	28·9	28·0	27·1	26·1	25·2	24·4	23·5	22·5	21·6	20·7	19·8
30	36·5	35·4	34·3	33·3	32·3	31·3	30·2	29·2	29·3	27·3	26·3	25·3	24·3
35	41·4	40·4	39·3	38·3	37·3	36·2	35·2	34·2	33·2	32·2	31·2	30·2	29·1
40	46·1	45·1	44·1	43·1	42·1	41·2	40·2	39·2	38·2	37·2	36·2	35·2	34·2
45	50·8	50·0	49·0	48·1	47·1	46·2	45·2	44·2	43·2	42·3	41·3	40·4	39·4
50	55·6	54·7	53·9	53·0	52·0	51·1	50·2	49·3	48·4	47·4	46·5	45·5	44·6
55	60·4	59·5	58·7	57·8	56·9	56·1	55·2	54·4	53·5	52·6	51·6	50·7	49·7
60	65·2	64·4	63·6	62·7	61·9	61·1	60·2	59·4	58·5	57·6	56·7	55·8	54·9
65	70·0	69·3	68·5	67·7	66·9	66·1	65·2	64·4	63·5	62·7	61·8	60·9	59·9
70	74·8	74·1	73·4	72·6	71·8	71·0	70·2	69·4	68·6	67·8	66·9	66·1	65·2
75	79·7	79·0	78·2	77·4	76·7	75·9	75·2	74·4	73·7	72·8	72·0	71·2	70·3
80	84·4	83·7	83·0	82·3	81·6	80·9	80·2	79·4	78·7	77·9	77·2	76·4	75·6
85	89·1	88·5	87·8	87·2	86·5	85·8	85·1	84·5	83·7	83·0	82·3	81·5	80·8
90	93·7	93·2	92·6	92·0	91·4	90·8	90·1	89·5	88·8	88·2	87·5	86·8	86·1
95	98·2	97·7	97·1	96·7	96·1	95·6	95·1	94·6	94·0	93·4	92·8	92·8	91·6
100	—	—	—	—	—	—	100·1	99·6	99·1	98·5	98·0	97·5	97·2

Table VI.—*Showing the Real Amount of Alcohol in Spirit at different Temperatures according to the indications of a glass Alcoholometer.*

Indications of the Alcoholometer.	Real Amount of Alcohol at the following Temperatures.											
	0° 0 32	2° 2·5 36·5	4° 5 41	6° 7·5 45·5	8° 10 50	10° 12·5 54·5	12° 15 59	14° 17·5 63·5	16° 20 68	18° 22·5 72·5	20° 25 77	22° 27·5 81·5	24° R. 30 C 86 F
0	0·3	0·4	0·4	0·4	0·4	0·2	—	—	—	—	—	—	—
5	5·4	5·5	5·5	5·5	5·4	5·2	5·0	4·7	4·4	4·1	3·7	3·2	2·5
10	11·1	11·1	11·0	10·9	10·7	10·4	10·1	9·7	9·2	8·7	8·3	7·8	7·3
15	17·7	17·4	17·1	16·4	16·0	15·5	15·1	14·5	14·0	13·4	12·8	12·2	11·5
20	24·9	24·0	23·1	22·4	21·7	21·0	20·2	19·5	18·8	18·0	17·2	16·4	15·6
25	31·3	30·2	29·2	28·2	27·2	26·2	25·2	24·3	23·4	22·5	21·6	20·7	19·8
30	37·0	35·7	34·6	33·4	32·4	31·3	30·2	29·2	28·2	27·2	26·2	25·2	24·2
35	42·0	40·7	39·6	38·5	37·4	36·2	35·2	34·1	33·1	32·1	31·0	30·0	28·9
40	46·6	45·5	44·5	43·4	42·3	41·2	40·2	39·1	38·0	37·0	36·0	35·0	33·9
45	51·5	50·4	49·4	48·3	47·3	46·2	45·2	44·2	43·1	42·1	41·1	40·0	39·0
50	56·3	55·3	54·3	53·3	52·3	51·2	50·2	49·2	48·2	47·1	46·1	45·0	44·0
55	61·2	60·2	59·2	58·2	57·2	56·2	55·2	54·2	53·2	52·2	51·2	50·2	49·2
60	66·2	65·2	64·2	63·2	62·2	61·2	60·2	59·2	58·2	57·2	56·3	55·3	54·3
65	71·1	70·1	69·1	68·1	67·2	66·2	65·2	64·2	63·3	62·3	61·3	60·3	59·3
70	76·0	75·0	74·1	73·1	72·1	71·1	70·2	69·3	68·3	67·3	66·4	65·4	64·4
75	80·9	79·9	79·0	78·1	77·1	76·1	75·2	74·3	73·3	72·3	71·4	70·4	69·4
80	85·7	84·9	83·9	83·0	82·0	81·1	80·2	79·3	78·3	77·4	76·4	75·5	74·5
85	90·5	89·6	88·8	87·9	87·0	86·1	85·2	81·3	83·4	82·4	81·5	80·6	79·6
90	95·0	94·1	93·5	92·7	91·9	91·0	90·2	89·3	88·4	87·5	86·8	85·7	84·8
95	99·5	98·6	98·0	97·1	96·5	95·8	95·2	91·3	93·5	92·7	91·9	91·1	90·2
100	—	—	—	—	—	100·8	100·2	99·6	99·0	98·3	97·6	96·9	95·7

The scale of Tralles' alcoholometer is constructed as follows. Suppose the cylindrical or prismatic stem of the instrument to be divided into a number of equal parts, of arbitrary length; and let v be the volume of that portion of the neck between two consecutive divisions; V the volume of liquid of sp. gr. 1, displaced by the alcoholometer, and P the weight of the alcoholometer; then

$$P = V \, . \, 1.$$

If now the division to which the instrument sinks in this liquid be marked 0, the divisions being numbered upwards therefrom, and if the instrument be immersed in spirit of specific gravity s to the mark n, we have

$$P = (V + n\,v)\,s,$$

which equations give,

$$V = (V + nv)\,s, \text{ or } n = \frac{V}{v}\left(\frac{1}{s} - 1\right) = \frac{V}{v} \cdot \frac{1-s}{s}$$

The arbitrary quantity v is fixed by Tralles at such a magnitude that

$$n = 10000 \cdot \frac{1-s}{s}$$

Now for 60° F. the specific gravity of water compared with that of water at its maximum density (Table I.) is 0·9991: hence for the division in which the instrument sinks in pure water at 60°, we find,

$$n = 10000 \cdot \frac{1-0{\cdot}9991}{0{\cdot}9991} = 9.$$

Again, spirit of 80 per cent. has at 60° F. the sp. gr. 0·8631: hence, for the division to which the instrument sinks therein, we have

$$n = 10000 \cdot \frac{1-0{\cdot}8631}{0{\cdot}8631} = 1587,$$

and in like manner the values of the other divisions of the scale may be found: they are given in Table VII.

To graduate an alcoholometer by means of this table, the instrument is first immersed in pure water at 60° F., and the point of the stem to which it sinks is marked 9. It is next immersed in spirit of known strength, and the point marked to which it sinks when the liquid is at 60° F. Thus if spirit of 90 per cent. be used, the number of the division will be

$$n = 10000 \cdot \frac{1-0{\cdot}8340}{0{\cdot}8340} = 2002.$$

The interval between these two marks is then to be divided into 2002 − 9 = 1993 equal parts, and the divisions continued upwards as far as 2597, which corresponds to absolute alcohol. The percentages in the first column of Table VII. are then marked on the scale by the side of the numbers of the divisions in the second column.

To verify the scale of an alcoholometer already divided, the specific gravities of a number of samples of spirit varying in strength by nearly equal intervals between 0 and 100 per cent. may be determined by any of the ordinary methods; the corresponding strength found from Tables I., II., or III.; the temperatures of them all then reduced to 60° F.; and the alcoholometer immersed in them in order to ascertain whether its indications agree with the strengths so determined. The intermediate points may be tested by comparison with the numbers in the columns of Table VII. marked "Differences."

TABLE VII.—*Alcoholometer-scale for Volumes per Cent. at 60° F.*

Amount of Alcohol by Volume.	Length of immersed part of Stem.	Differences.	Amount of Alcohol by Volume.	Length of immersed part of Stem.	Differences.	Amount of Alcohol by Volume.	Length of immersed part of Stem.	Differences.
0	9		22	277	11	44	588	19
1	24	15	23	288	11	45	608	20
2	39	15	24	299	11	46	628	20
3	54	15	25	310	11	47	648	20
4	68	14	26	321	11	48	669	21
5	82	14	27	332	11	49	690	21
6	95	13	28	344	12	50	712	22
7	108	13	29	355	11	51	735	23
8	121	13	30	367	12	52	758	23
9	133	12	31	380	13	53	782	24
10	145	12	32	393	13	54	806	24
11	157	12	33	407	14	55	830	24
12	169	12	34	420	13	56	854	24
13	180	11	35	434	14	57	879	25
14	191	11	36	449	15	58	905	26
15	202	11	37	465	16	59	931	26
16	213	11	38	481	16	60	957	26
17	224	11	39	498	17	61	984	27
18	235	11	40	515	17	62	1011	27
19	245	10	41	533	18	63	1039	28
20	256	10	42	551	18	64	1067	28
21	266	10	43	569	18	65	1096	29

TABLE VII—(*continued*).

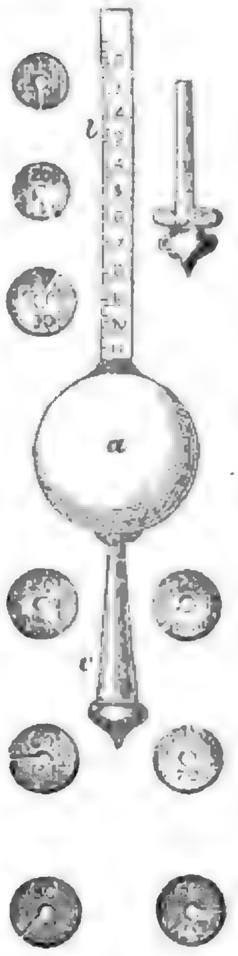
Amount of Alcohol by Volume.	Length of immersed part of Stem.	Differences.	Amount of Alcohol by Volume.	Length of immersed part of Stem.	Differences.	Amount of Alcohol by Volume.	Length of immersed part of Stem.	Differences.
66	1125	29	78	1514	36	90	2002	47
67	1154	29	79	1550	36	91	2050	48
68	1184	30	80	1587	37	92	2099	49
69	1215	31	81	1624	37	93	2150	51
70	1246	31	82	1662	38	94	2203	53
71	1278	32	83	1701	39	95	2259	56
72	1310	32	84	1740	39	96	2318	59
73	1342	32	85	1781	41	97	2380	62
74	1375	33	86	1823	42	98	2447	67
75	1409	34	87	1866	43	99	2519	72
76	1443	34	88	1910	44	100	2597	78
77	1478	35	89	1955	45			

The following is a similar table for percentages by weight.

TABLE VIII.—*Alcoholometer-scale for Weights per Cent. at 60° F.*

Amount of Alcohol by Weight	Length of immersed part of Stem.	Differences.	Amount of Alcohol by Weight.	Length of immersed part of Stem.	Differences.	Amount of Alcohol by Weight.	Length of immersed part of Stem.	Differences.
0	9	—						
1	28	19	35	547	20	68	1411	31
2	46	18	36	568	21	69	1442	31
3	64	18	37	589	21	70	1473	31
4	82	18	38	610	21	71	1505	32
5	98	16	39	633	22	72	1536	31
6	114	16	40	655	22	73	1568	32
7	130	16	41	677	22	74	1600	32
8	145	15	42	700	23	75	1632	32
9	159	14	43	724	24	76	1664	32
10	173	14	44	748	24	77	1697	33
11	187	14	45	772	24	78	1730	33
12	201	14	46	797	25	79	1763	33
13	214	13	47	822	25	80	1796	33
14	227	13	48	847	25	81	1830	34
15	240	13	49	873	26	82	1865	35
16	252	12	50	899	26	83	1901	36
17	264	12	51	925	26	84	1938	37
18	277	13	52	951	26	85	1975	37
19	291	14	53	978	27	86	2012	37
20	304	13	54	1005	27	87	2050	38
21	317	13	55	1033	28	88	2088	38
22	330	13	56	1061	28	89	2126	38
23	343	13	57	1089	28	90	2165	39
24	357	14	58	1117	28	91	2204	39
25	371	14	59	1145	28	92	2254	40
26	386	15	60	1173	28	93	2286	42
27	402	16	61	1202	29	94	2329	43
28	419	17	62	1231	29	95	2372	43
29	435	16	63	1261	30	96	2415	43
30	452	17	64	1290	29	97	2458	43
31	469	17	65	1320	30	98	2503	45
32	487	18	66	1350	30	99	2549	46
33	507	20	67	1380	30	100	2597	48
34	527	20						

Fig. 3.



Various other hydrometers or areometers are also used for taking the specific gravity and ascertaining the strength of spirits. Sikes's hydrometer is the one used in levying the spirit duty in this country. This instrument has a four-sided stem *b*, divided into 11 equal parts, and fitting into a brass ball *a*, which carries at the bottom a small conical stem *c*, terminating in a pear-shaped loaded bulb. It is also provided with 9 circular weights, numbered 10, 20, 30, 40, 50, 60, 70, 80, 90, having slits by which they fit into the stem. The instrument is adjusted so as to float with the zero of the scale coinciding with the surface of the liquid in spirit of specific gravity 0·825 at 60°F. which is the "*standard alcohol*" of the excise (p. 82). In weaker spirit it will not sink so low; and if the density of the liquid be much greater, it will be necessary to add one or more of the weights, to cause the entire immersion of the bulb. The sum of the numbers of the weights together with the number on the scale which is at the level of the liquid, gives, by means of a table provided for the purpose, the amount of *proof spirit* in the sample, proof spirit being, according to Act of Parliament, such as at 51° Fahr. weighs $\frac{12}{13}$ as much as an equal bulk of water, or in other words has a specific gravity of 0·923077 at 51°, or 0·919 at 60° F.

When spirit is said to be 30 per cent. (for example) *above proof*, the meaning is, that 100 measures of this spirit, when diluted with water, would yield 130 measures of proof spirit; on the other hand, spirit 30 per cent. *below proof* contains in 100 measures, 100 − 30 or 70 measures of proof spirit.

It is often required to find the quantity of water which must be added to spirit containing a given percentage of alcohol in order to reduce it to a lower percentage. If the actual and required amounts are given in weights per cent., a and a', the weight x of water to be added to 100 lbs of spirit to reduce the percentage of alcohol from a to a', is given by the proportion:

$$100 + x : a = 100 : a',$$

$$\text{whence } x = 100\left(\frac{a}{a'} - 1\right)$$

If, for example. spirit containing 90 lbs. of alcohol in 100 lbs. is to be reduced to spirit containing 60 lbs. per cent., the quantity of water required is

$$100\left(\frac{90}{60} - 1\right) = 100 \times 0{\cdot}5 = 50 \text{ lbs.}$$

Next, let it be required to find what volume of water must be added to 100 volumes of spirit containing v volumes per cent. of alcohol to reduce it to v' volumes per cent.

If P be the weight, and S the specific gravity of the spirit we have:

$$P = 100\,S.$$

and if to this we add w volumes of water, the weight of which will also be w (its specific gravity being 1), we obtain a volume V of spirit, whose specific gravity may be denoted by S', and its amount of alcohol in volumes per cent. by v'. Then,

$$P + w = 100\,S + w = VS',$$

$$\text{and} \qquad V : 100 = v : v',$$

$$\text{or,} \qquad V = 100 \cdot \frac{v}{v'},$$

because the diluted spirit still contains the v volumes of alcohol which were present in the liquid before dilution. From these two equations we find

$$w = 100\left(\frac{v}{v'}\,S' - S\right)$$

For example, to reduce spirit of 80 volumes p. c. to spirit of 40 volumes p. c. we find,

$$w = 100 \cdot \left(\frac{80}{40} \cdot 0{\cdot}9519 - 0{\cdot}8639\right) = 103{\cdot}99$$

so that 100 measures of the given spirit require 103·99 measures of water at 60°F. to reduce them from 80 to 40 per cent.

The volume of diluted spirit produced by the mixture is

$$v = 100\,\frac{v}{v'}$$

In the example just given, $100 \cdot \frac{80}{40} = 200$ volumes, less therefore than the sum of the volumes of the liquids mixed.

On the principles just explained, the numbers in the following table are calculated. It must be observed, however, that the specific gravities are given as determined by Gay-Lussac, and correspond to 15° C. on which account the result of the calculation just given does not agree exactly with the number in the table.

The original volumes per cent. of the spirit are placed at the tops of the columns, and the percentages to which they are to be reduced in the first column of the table. Thus to find how much water is required to reduce spirit of 75 per cent. to 40 per cent. look in the column headed 70 for the number on a level with 40 in the first column; we thus find that 77·58 volumes is the quantity of water required:

Table IX.—*Showing the quantity of Water required to reduce* 100 *volumes of a stronger Spirit to a Spirit of lower strength.*

	90	85	80	75	70	65	60	55	50
85	6·56								
80	13·79	6·83							
75	21·89	14·48	7·20						
70	31·05	23·14	15·35	7·64					
65	41·53	33·03	24·66	16·37	8·15				
60	53·65	44·48	35·44	26·47	17·58	8·76			
55	67·87	57·90	48·07	38·32	28·63	19·02	9·47		
50	84·71	73·90	63·04	52·43	41·73	31·25	20·47	10·35	
45	105·34	93·30	81·38	69·54	57·78	46·09	34·46	22·90	11·41
40	130·80	117·34	104·01	90·76	77·58	64·48	51·43	38·46	25·55
35	163·28	148·01	132·88	117·82	102·84	87·93	73·08	58·31	43·59
30	206·22	188·57	171·05	103·53	136·04	118·94	101·71	84·54	67·45
25	266·12	245·15	224·30	253·61	182·83	162·21	141·65	121·16	100·73
20	355·80	329·84	304·01	278·26	252·58	226·98	201·43	175·96	150·55
15	505·27	471·00	436·85	402·81	368·83	334·91	301·07	267·29	233·64
10	804·54	753·65	702·89	651·21	601·60	551·06	500·59	450·19	399·85

A similar but much more extended table for this purpose is given by Gay-Lussac. (See Handworterbuch d. Chem. i. 504.)

To determine what quantity of a weaker spirit must be added to a stronger one to produce a spirit of given mean percentage, we proceed as follows.

Let v be the volume of alcohol in 100 measures of the stronger spirit, S its specific gravity, and P its weight. Also let V_1 be the volume of the weaker spirit added, v_1 its percentage of alcohol, S_1 its specific gravity, and P_1 its weight; and lastly, let V_2 be the volume of spirit resulting from the mixture, v_2 its percentage of alcohol, S_2 its specific gravity, and P_2 its weight. Then:

$$P = 100\,S \;:\; P_1 = V_1 S_1 \;:\; P_2 = P + P_1$$

$$\text{or } 100\,S + V_1 S_1 = V_2 S_2 \quad . \quad . \quad . \quad (1).$$

The quantity of alcohol contained in this mixture is,

$$v + \frac{V_1}{100}\,v_1$$

But since the mixed spirit is to contain V_2 volumes per cent. of alcohol, this quantity of alcohol is also represented by

$$\frac{V_2}{100}\,v_2$$

Hence the equation:

$$V_2 v_2 = 100\,v + V_1 v_1 \,. \quad . \quad . \quad (2).$$

And eliminating V_2 between the equations (1) and (2), we have,

$$\frac{100\,S + V_1 S_1}{S_2}\,v_2 = 100\,v + V_1 v_1$$

whence we obtain:

$$V = \frac{100\,\frac{v}{v_2}\,S - 100\,S}{S_1 - \frac{v_1}{v_2}\,S_2}$$

The numerator of this fraction is the quantity of water which must be added to 100 volumes of the stronger spirit to produce a spirit of the required strength. The denominator may be written in the form,

$$\frac{v_1}{v_2}\left(\frac{v_2}{v_1}\,S_1 - S_2\right)$$

and is therefore the volume of water which must be added to $\frac{v_1}{v_2}$ volumes of spirit containing v_2 per cent. of alcohol to bring it to the percentage v_1.

To determine the amount of alcohol in spirituous liquors, such as wine or beer, containing foreign matters, as volatile oils, sugar, mucilage, saline substances, &c., the liquid may be distilled, and the distillate, which will be free from the fixed impurities, may be treated by the methods already described. Volatile oils are for the most part of nearly the same specific gravity as alcohol, and the small quantities of them existing in vinous liquors do not make any essential difference in the specific gravity.

Other physical characters have also been resorted to for determining the strength of spirituous liquors, viz. the boiling-point, vapour-density, rate of expansion, &c.

The *boiling-point* of hydrated alcohol has been proposed by Gröning as a means of determining its strength. For this purpose, he has constructed the following table.

Per Cent. of Alcohol.	Boiling-Point.	Per Cent. of Alcohol.	Boiling-Point.	Per Cent. of Alcohol.	Boiling-Point.
5	96·3 C.	40	84·1 C.	70	80·9 C.
10	92·9	45	83·4	75	80·3
15	91·0	50	83·1	80	79·7
20	89·1	50	82·2	85	79·4
25	87·5	60	81·9	90	79·0
30	86·2	65	81·5	95	78·4
35	85·0				

According to Dalton, alcohol of 43 per cent. boils at 84° C.

J. J. Pohl (Denkschriften d. math. naturw. Classe d. Wien, Akad. II. abstr. Wien, Akad. Ber. 1850; Marz. 246; Jahresber. 1850, 455) has also determined the boiling-point of hydrated alcohol of various strengths. He finds that, at the commencement of the ebullition, the thermometer remains constant for a short time, then slowly rises a little, and afterwards remains constant for a somewhat longer time (from 4 to 16 seconds when 14·6 grms. of liquid were used). The temperatures at the second stationary interval are given in the following table (Bar. at 760 mm.)

Percentage of Alcohol.	Boiling-Point.	Percentage of Alcohol.	Boiling-Point.
0	100·00° C.	7	93·43° C.
1	98·79	8	92·70
2	97·82	9	92·03
3	96·85	10	91·40
4	95·90	11	90·83
5	95·02	12	90·27
6	94·21		

The presence of sugar in the liquid up to 15 p. c. appears not to exert any perceptible influence on the boiling-point (a mixture of 10 pts. alcohol with 15 sugar and 75 water boiled at the same temperature as a mixture of 10 alcohol and 90 water).

Instruments, called *Ebullioscopes*, for directly ascertaining the strength of hydrated alcohol by its boiling-point, have been constructed by Broissard-Vidal and by Conaty. (See a report on these instruments by Despretz, Pouillet, and Babinet, Compt. rend. xxvii. 374. A description and figure of a Vidal-instrument are given in the Pharm. J. Trans. vii. 166.) Ure (Pharm. J. Trans. vii. 166; Pharm. Centr. 1847, 422) by means of an instrument similar to Conaty's (which is merely an ordinary thermometer, having a moveable scale which can be shifted so as to correspond with the variations of the barometer, and has the percentages of alcohol marked on it) has determined the boiling-points of hydrated alcohol as follows:

Specific Gravity.	Boiling-Point.	Specific Gravity.	Boiling-Point.
0·9200	81·4° C.	0·9665	85·3° C.
0·9321	82·1	0·9729	87·2
0·9420	82·5	0·9786	88·8
0·9516	83·3	0·9850	91·3
0·9600	84·1	0·9920	94·4

Silbermann has proposed to determine the strength of hydrated alcohol by its rate of expansion by heat, and has constructed an instrument for the purpose (Compt. rend. xxvii. 418). A thermometer is filled up to a certain mark with the spirit at 25° C. and after this liquid has been exhausted of air by the air-pump, an observation is made of the amount by which it expands when heated to 50° C. The amount of alcohol is then found by means of a scale graduated by direct observation upon a number of samples of spirit of known strength. The indications of this instrument are not sensibly affected by the presence of sugar or salts in the liquid.

Another instrument for the same purpose has been constructed and described by Makin. (Chem. Soc. Qu. J. ii. 224.)

For further details on alcoholometry, see the new edition of *Ure's Dictionary of Arts, Manufactures and Mines*, vol. i. pp. 44-64.

ALCOHOL-RADICLES. The radicles which, when they replace half the hydrogen in a molecule of water form alcohols, are capable of uniting, though not directly, with chlorine bromine, iodine, cyanogen, oxygen, sulphur, &c., with the radicles of acids, and with metals: in short they exhibit in their chemical relations the character of electro-positive elements or metals. Only a few of them have yet been isolated; and of these, all but one (allyl) belong to the first series of alcohols mentioned in the preceding article, and are represented by the general formula C^nH^{2n+1}, or $C^{2n}H^{4n+2}$. They are obtained:

1. By the action of sodium, potassium, zinc, &c., at high temperatures, on their iodides or bromides. In this manner ethyl was first isolated by Frankland.—2. By the electrolysis of the acids of the series $C^nH^{2n}O^2$. The general formula of the decomposition is,

$$C^nH^{2n}O^2 = C^{n-1}H^{2n-1} + CO^2 + H.$$

In this manner, acetic acid, $C^2H^4O^2$, yields methyl, CH^3; valeric acid, $C^5H^{10}O^2$, yields tetryl or butyl, C^4H^9; caproic acid, $C^6H^{12}O^2$, yields amyl, C^5H^{11}; and œnanthylic acid $C^7H^{14}O^2$ yields hexyl or caproyl, C^6H^{13}.—3. Some of these radicles, viz. trityl or propyl, tetryl, amyl and hexyl, are also found among the products of the dry distillation of Boghead Cannel coal. (Gr. Williams, Chem. Gaz. 1857, pp. 29 and 95.)

Methyl and ethyl are gaseous at ordinary temperatures; trityl, tetryl, amyl, and hexyl, are liquids, the first boiling at 68° C, the second at 108°, the third at 155°, and and the fourth at 202°. They do not unite directly with any of the elementary bodies, and it has not yet been found possible to reproduce from them, by direct union, any of the bodies of the methyl, ethyl series, &c. At the moment of isolation, however, from their iodides by the action of metals, they exhibit a strong tendency to unite with the metal: in this manner, zinc-ethyl, C^2H^5Zn and zinc-methyl, C^2H^3Zn, are formed by the action of zinc on the iodides of those radicles.

The constitution of these bodies has given rise to considerable discussion. The formulæ CH^3, C^2H^5, &c., originally assigned to them by Frankland and Kolbe, represent their vapours as condensed to 1 volume, whereas the usual mode of condensation in organic compounds is to 2 volumes (see ATOMIC VOLUME). For this reason, and likewise because all organic compounds whose formulæ are well established, are found to contain even numbers of hydrogen-atoms, Gerhardt (Compt. chim. 1848, 19; 1849, 11) proposed to double the formulæ of these radicles in the free state, making them C^2H^6 or $\left.\begin{matrix}CH^3\\CH^3\end{matrix}\right\}$, C^4H^{10} or $\left.\begin{matrix}C^2H^5\\C^2H^5\end{matrix}\right\}$ &c. This duplication of the formulæ was afterwards supported by Hofmann (Chem. Soc. J. iii. 121) on the ground that the boiling-points of the consecutive terms of the series of these bodies differ by about 47° C., an interval more than double of that which generally corresponds to a difference of CH^2 in bodies of the methyl, ethyl, trityl series, &c. But the decisive argument in favour of the double formulæ is afforded by the experiments of Wurtz, who has shown that by the action of mixtures of the iodides of these radicles (iodide of ethyl and iodide of tetryl, for example) with sodium, or by the electrolysis of a mixture of the potassium-salts of two fatty acids, *e. g.* acetate and œnanthylate of potassium, compound radicles are obtained, viz. ethyl-tetryl, $\left.\begin{matrix}CH^3\\C^4H^9\end{matrix}\right\}$, methyl-hexyl $\left.\begin{matrix}CH^3\\C^6H^{13}\end{matrix}\right\}$ &c.; and moreover that when these mixed radicles are compared with the simple radicles with double formulæ, a regular gradation of physical properties is observed as the number of atoms in the molecule increases. This will be seen from the following table.

Radicle.	Formula.	Specific Gravity at 0° C.	Vapour-Density		Boiling Point.
			Observed.	Calculated.	
Ethyl-tetryl .	$C^6H^{14} = \left\{\begin{matrix}C^2H^5\\C^4H^9\end{matrix}\right.$	0·7011	3·053	2·972	62°
Ethyl-amyl .	$C^7H^{16} = \left\{\begin{matrix}C^2H^5\\C^5H^{11}\end{matrix}\right.$	0·7069	3·522	3·455	88°
Methyl-hexyl .	$C^7H^{16} = \left\{\begin{matrix}CH^3\\C^6H^{13}\end{matrix}\right.$	?	3·426	3·455	82 ?
Tetryl . .	$C^8H^{18} = \left\{\begin{matrix}C^4H^9\\C^4H^9\end{matrix}\right.$	0·7057	4·070	3·939	106
Tetryl-amyl .	$C^9H^{20} = \left\{\begin{matrix}C^4H^9\\C^5H^{11}\end{matrix}\right.$	0·7247	4·465	4·423	132
Amyl . .	$C^{10}H^{22} = \left\{\begin{matrix}C^5H^{11}\\C^5H^{11}\end{matrix}\right.$	0·7413	4·956	4·907	158
Tetryl-hexyl .	$C^{10}H^{22} = \left\{\begin{matrix}C^4H^9\\C^6H^{13}\end{matrix}\right.$	?	4·917	4·907	155
Hexyl . .	$C^{12}H^{26} = \left\{\begin{matrix}C^6H^{13}\\C^6H^{13}\end{matrix}\right.$	0·7574	5·983	5·874	202

It is clear that if the simpler formulæ of tetryl, amyl and hexyl were retained, accordance between the gradation of properties and increase of atomic weight wh the preceding table exhibits would be completely lost.

Viewed in this light, the formation of the simple radicles is strictly analogou that of the mixed radicles, as will be seen from the following equations:

$$C^2H^5I + C^4H^9I + ZnZn = 2ZnI + C^2H^5.C^4H^9$$

and

$$2C^2H^5I + ZnZn = 2ZnI + C^2H^5.C^2H^5.$$

ALCOHOLS. The term alcohol, originally limited to one substance, viz. spiri wine, is now applied to a considerable number of organic compounds, many of wh in their external characters, exhibit but little resemblance to common alcohol. alcohols are all compounds of carbon, hydrogen, and oxygen. They are divided several homologous groups, but their rational formulæ may all be derived from two, or three molecules of water, $\left.\begin{matrix}H\\H\end{matrix}\right\}O$, $\left.\begin{matrix}H^2\\H^2\end{matrix}\right\}O^2$, $\left.\begin{matrix}H^3\\H^3\end{matrix}\right\}O^3$, by substitution of an ganic radicle containing hydrogen and carbon for half the hydrogen in the t Alcohols are accordingly monatomic, diatomic, or triatomic, *e.g.* Ethyl-alco (monatomic) = $\left.\begin{matrix}C^2H^5\\H\end{matrix}\right\}O$, — Glycol (diatomic) = $\left.\begin{matrix}(C^2H^4)''\\H^2\end{matrix}\right\}O^2$, — Glycerin (t tomic) = $\left.\begin{matrix}(C^3H^5)'''\\H^3\end{matrix}\right\}O^3$

A. **Monatomic Alcohols.** Of these there are several series, containing rad whose general formulæ are C^nH^{2n+1}, C^nH^{2n-1}, C^nH^{2n-3}, C^nH^{2n-7}.

1. Alcohols of the form $C^nH^{2n+2}O = \left.\begin{matrix}C^nH^{2n+1}\\H\end{matrix}\right\}O$. These alcohols, of w nine, or perhaps ten, are at present known, are intimately related to the fatty acid 50). To every alcohol of this series there corresponds an acid of the series C^nH^2 which may be formed from the alcohol by oxidation, O being substituted for H^2. following table exhibits the names and formulæ of these alcohols, together with t of those of the corresponding acids:

Alcohols, $\left.\begin{matrix}C^nH^{2n+1}\\H\end{matrix}\right\}O$		Acids, $\left.\begin{matrix}C^nH^{2n-1}O\\H\end{matrix}\right\}O$	
Methylic or protylic . . .	CH^4O	Formic	CH^2
Ethylic or deutylic . . .	C^2H^6O	Acetic	C^2H
Propylic or tritylic . . .	C^3H^8O	Propionic	C^3H
Butylic or tetrylic . . .	$C^4H^{10}O$	Butyric	C^4H
Amylic or pentylic . . .	$C^5H^{12}O$	Valeric	C^5H
Caproylic or hexylic . . .	$C^6H^{14}O$	Caproic	C^6H
Œnanthylic or heptylic . .	$C^7H^{16}O$	Œnanthylic	C^7H
Caprylic or octylic . . .	$C^8H^{18}O$	Caprylic	C^8H
Cetylic	$C^{16}H^{34}O$	Palmitic	C^{16}
Cerotylic	$C^{27}H^{56}O$	Cerotic	C^{27}
Melissylic	$O^{30}H^{62}O$	Melissic	C^{30}

These alcohols are also designated as *Hydrates*, or *Hydrated Oxides, of Methyl, Ethyl*, &c., or as *Methylate, Ethylate, Tritylate, &c.* of *Hydrogen*. The numerical terms *protyl, deutyl, trityl*, &c. were proposed by Gerhardt. They are in most cases preferable to the older names: but the terms, methyl, ethyl, and amyl, are too much consecrated by use to be discarded.

Methyl-alcohol, or wood-spirit, was first recognised as a compound similar in nature and constitution to common alcohol by Dumas and Peligot in 1835. In the following year, the same chemists showed that ethal (cetyl-alcohol), a substance first obtained from spermaceti by Chevreul in 1823, is also of alcoholic nature. Fusel-oil was recognised as an alcohol somewhat later by Cahours and Balard. Cerotyl-alcohol and melissyl-alcohol were discovered by Brodie in 1848; octyl-alcohol by Bouis in 1851; tetryl-alcohol by Wurtz in 1852; trityl-alcohol by Chancel in 1852, and hexyl-alcohol by Faget in the same year.

Methyl-alcohol is found among the products of the distillation of wood. *Ethyl-alcohol* and the four following alcohols are produced by fermentation of sugar, ($C^6H^{12}O^6$), perhaps in the manner represented by the following equations:

$$C^6H^{12}O^6 = \underset{\substack{\text{Ethyl-}\\\text{alcohol.}}}{2C^2H^6O} + 2CO^2$$

$$2C^6H^{12}O^6 = \underset{\substack{\text{Trityl-}\\\text{alcohol.}}}{2C^3H^8O} + \underset{\substack{\text{Ethyl-}\\\text{alcohol.}}}{C^2H^6O} + 4CO^2 + H^2O$$

$$C^6H^{12}O^6 = \underset{\substack{\text{Tetryl-}\\\text{alcohol.}}}{C^4H^{10}O} + 2CO^2 + H^2O$$

$$3C^6H^{12}O^6 = \underset{\substack{\text{Amyl-}\\\text{alcohol.}}}{2C^5H^{12}O} + \underset{\substack{\text{Ethyl-}\\\text{alcohol.}}}{C^2H^6O} + 6CO^2 + 3H^2O$$

$$2C^6H^{12}O^6 = \underset{\substack{\text{Amyl-}\\\text{alcohol.}}}{C^5H^{12}O} + \underset{\substack{\text{Trityl-}\\\text{alcohol.}}}{C^3H^8O} + 4CO^2 + 2H^2O$$

$$5C^6H^{12}O^6 = \underset{\substack{\text{Amyl-}\\\text{alcohol.}}}{4C^5H^{12}O} + 10CO^2 + 6H^2O$$

$$3C^6H^{12}O^6 = \underset{\substack{\text{Hexyl-}\\\text{alcohol.}}}{2C^6H^{14}O} + 6CO^2 + 4H^2O$$

Octyl-alcohol is said to be obtained by saponifying castor-oil with potash, and distilling the resulting ricinolate of potassium with excess of the alkali at a high temperature. The ricinolic acid is then converted into octyl-alcohol, sebate of potassium, and free hydrogen:

$$\underset{\substack{\text{Ricinolic}\\\text{acid.}}}{C^{18}H^{34}O^3} + 2KHO = \underset{\substack{\text{Octyl-}\\\text{alcohol.}}}{C^8H^{18}O} + \underset{\substack{\text{Sebate of}\\\text{potassium.}}}{C^{10}H^{16}K^2O^4} + 2H$$

Bouis (Compt. rend. xxiii. 141). Other chemists, however, who have examined this reaction, state that the alcohol produced by it is not octylic, but heptylic. According to **Städeler** (J. pr. Chem. lxxii. 241) two reactions take place simultaneously, the one giving rise to the formation of heptylic alcohol, sebate of potassium, and hydride of methyl (marsh gas), the other to the formation of *methyl-œnanthyl*, an acetone isomeric with caprylic aldehyde, $C^8H^{16}O$, and free hydrogen; thus:

$$\underset{\substack{\text{Ricinolic}\\\text{acid.}}}{C^{18}H^{34}O^3} + 2KHO = \underset{\substack{\text{Heptyl-}\\\text{alcohol.}}}{C^7H^{16}O} + \underset{\substack{\text{Sebate of}\\\text{potassium.}}}{C^{10}H^{16}K^2O^4} + \underset{\substack{\text{Hydride}\\\text{of methyl.}}}{CH^3.H}$$

$$\underset{\substack{\text{Ricinolic}\\\text{acid.}}}{C^{18}H^{34}O^3} + 2KHO = \underset{\substack{\text{Methyl-}\\\text{œnanthyl.}}}{CH^3.C^7H^{13}O} + \underset{\substack{\text{Sebate of}\\\text{potassium.}}}{C^{10}H^{16}K^2O^4} + H^4$$

According to **Dachauer**, on the contrary (Ann. Ch. Pharm. cvi. 270), the products of the distillation are methyl-œnanthyl and octylic alcohol, the formation of this alcohol differing from that of methyl-œnanthyl only by the elimination of two atoms of hydrogen instead of four. It does not appear that Städeler actually observed the evolution of marsh gas.

Cetyl-alcohol (or ethal) is obtained by decomposing spermaceti (which consists chiefly of *cetin*, $C^{32}H^{64}O^2$) with alkalis, palmitic acid being formed at the same time:

$$\underset{\text{Cetin.}}{C^{32}H^{64}O^2} + KHO = \underset{\substack{\text{Cetyl-}\\\text{alcohol.}}}{C^{16}H^{34}O} + \underset{\substack{\text{Palmitate of}\\\text{potassium.}}}{C^{16}H^{31}KO^2}$$

In the same manner, cerotyl-alcohol is formed from Chinese-wax, and melissyl-alcohol from bees-wax.

$$\underset{\text{Chinese-wax.}}{C^{54}H^{108}O^2} + KHO = \underset{\text{Cerotyl-alcohol.}}{C^{27}H^{56}O} + \underset{\text{Cerotate of potassium.}}{C^{27}H^{53}KO^2}$$

Some of these alcohols have also been formed from the corresponding hydrocarbons C^nH^{2n}, *e.g.* common alcohol from olefiant gas, C^2H^4, and trityl-alcohol from tritylene, C^3H^6, by dissolving these gaseous hydrocarbons in strong sulphuric acid, and decomposing the resulting ethyl-sulphuric or trityl-sulphuric acid by distillation with water. Methyl-alcohol has been formed from marsh-gas, CH^4, by exposing that compound to the action of chlorine in sunshine, whereby chloride of methyl is obtained, and decomposing this body with aqueous potash (Berthelot, Compt. rend. xlv. 916):

$$CH^3Cl + KHO = CH^4O + KCl.$$

The first eight alcohols of the series are liquid at ordinary temperatures. Methylic and ethylic alcohols are mobile watery liquids; the others are more or less oily, the viscidity increasing with the atomic weight. Cetyl-alcohol is a solid fat: cerotylic and melissylic alcohols are waxy.

Oxidising agents convert these alcohols into aldehydes, $C^nH^{2n}O$, or acids, $C^nH^{2n}O^2$, in each case with elimination of one atom of water:

$$C^nH^{2n+2}O + O = C^nH^{2n}O + H^2O$$

and

$$C^nH^{2n+2}O + O^2 = C^nH^{2n}O^2 + H^2O$$

These changes take place on exposing the alcohols to the air, especially in contact with platinum-black, and more quickly on distilling them with a mixture of dilute sulphuric acid and chromate of potassium. The alcohols are also converted into fatty acids by heating them strongly in contact with soda-lime (a mixture of quick lime with caustic soda); *e.g.* amyl-alcohol thus treated yields valerate of sodium.

The alcohols of this series contain one atom of hydrogen replaceable by metals or compound radicles. Many of them, when treated with potassium or sodium, give off hydrogen, and form solid compounds containing 1 atom of the alkali-metal, *e.g.* ethylate of sodium, C^2H^5NaO. In this respect the alcohols partake of the nature of acids.—The compounds thus formed are easily decomposed, and are not easily obtained in a definite form.

On treating these potassium- or sodium-alcohols with the iodide of an alcohol-radicle, iodide of potassium or sodium is precipitated, and an *ether* is formed, that is to say, a compound derived from an alcohol by the substitution of an alcohol-radicle for the basic atom of hydrogen: thus ethylate of sodium with iodide of ethyl yields ethylic ether $(C^2H^5)^2O$, and with iodide of amyl, ethyl-amyl ether, $C^2H^5.C^5H^{11}.O$ (p. 76).

The alcohols are also converted into ethers by the action of strong sulphuric acid chloride of zinc, fluoride of boron, and other powerful dehydrating agents, at a certain temperature. The *ultimate* change is represented by the equation:

$$\underbrace{2\left(\left.\begin{matrix}C^nH^{2n+1}\\H\end{matrix}\right\}O\right)}_{\text{Alcohol.}} - H^2O = \underbrace{\left.\begin{matrix}C^nH^{2n+1}\\C^nH^{2n+1}\end{matrix}\right\}O}_{\text{Ether.}}$$

For the intermediate steps of the process see page 76. This particular change takes place only between certain limits of temperature, *e.g.* for the etherification of common alcohol by sulphuric acid, the limits are 140° and 160° C. At higher temperatures, a further dehydration takes place, and a hydrocarbon C^nH^{2n} is obtained:

$$C^nH^{2n+2}O - H^2O = C^nH^{2n}$$

e.g. common alcohol heated above 160° with strong sulphuric acid, yields olefiant gas C^2H^4.

With the greater number of acids, alcohols yield *compound ethers*; that is to say, salts in which the basic hydrogen of the acid is more or less replaced by the radicle of the alcohol. With monobasic acids, only neutral ethers are formed: thus common alcohol heated with strong acetic acid yields acetate of ethyl, with elimination of water:

$$\left.\begin{matrix}C^2H^5\\H\end{matrix}\right\}O + \left.\begin{matrix}C^2H^3O\\H\end{matrix}\right\}O = \left.\begin{matrix}C^2H^3O\\C^2H^5\end{matrix}\right\}O + H^2O$$

The formation of these ethers is greatly assisted by the presence of strong sulphuric or hydrochloric acid, to take up the water. They are commonly prepared either by distilling the alcohol with sulphuric acid, and a salt of the other acid (*e.g.* acetate of ethyl, by distilling alcohol with sulphuric acid and acetate of sodium), or by passing hydrochloric acid gas into an alcoholic solution of the acid. The former method is applicable to the more volatile ethers, the latter to those of higher boiling-point.

With dibasic and tribasic acids, the alcohols generally form *acid ethers* or *alcoholic acids*, that is to say, compounds in which only a portion of the basic hydrogen of the acid is replaced by the alcohol-radicle. Thus, when amyl-alcohol is mixed with sulphuric acid and the mixture kept cool, *amyl-sulphuric acid*, $\left.\begin{matrix}C^5H^{11}\\H\end{matrix}\right\}SO^4$ or $\left.\begin{matrix}(SO^2)''\\C^5H^{11}.H\end{matrix}\right\}O^2$ is produced:

$$\left.\begin{matrix}C^5H^{11}\\H\end{matrix}\right\}O \;+\; \left.\begin{matrix}H\\H\end{matrix}\right\}SO^4 = \left.\begin{matrix}C^5H^{11}\\H\end{matrix}\right\}SO^4 + \left.\begin{matrix}H\\H\end{matrix}\right\}O$$

In like manner, phosphoric acid and amyl-alcohol yield amyl-phosphoric acid, $PO^4.C^5H^{11}.H^2$.

Hydrochloric, hydrobromic, and hydriodic acids convert the alcohols of this series into chlorides, &c., of the alcohol-radicles, with elimination of water:

$$\left.\begin{matrix}C^nH^{2n+1}\\H\end{matrix}\right\}O + HCl = C^nH^{2n+1}\,Cl + H^2O$$

A similar transformation is effected by the chlorides, bromides, and iodides of phosphorus: *e.g.*

$$\underbrace{\left.\begin{matrix}C^5H^{11}\\H\end{matrix}\right\}O}_{\substack{\text{Amyl-}\\\text{alcohol.}}} + \underbrace{PCl^3.Cl^2}_{\substack{\text{Penta-}\\\text{chloride of}\\\text{phosphorus.}}} = \underbrace{C^5H^{11}Cl}_{\substack{\text{Chloride}\\\text{of amyl.}}} + HCl + \underbrace{POCl^3}_{\substack{\text{Oxychlo-}\\\text{ride of}\\\text{phosphorus.}}}$$

With the chlorides of acid radicles, the alcohols form compound ethers, hydrochloric acid being at the same time eliminated:

$$\underbrace{\left.\begin{matrix}C^2H^5\\H\end{matrix}\right\}O}_{\substack{\text{Ethyl-}\\\text{alcohol.}}} + \underbrace{C^7H^5O.Cl}_{\substack{\text{Chloride of}\\\text{benzoyl.}}} = \underbrace{\left.\begin{matrix}C^7H^5O\\C^2H^5\end{matrix}\right\}O}_{\substack{\text{Benzoate}\\\text{of ethyl.}}} + HCl$$

Persulphide of phosphorus transforms the alcohols of this series into mercaptans (sulphur-alcohols):

$$5C^nH^{2n+2}\,O + P^2S^5 = 5C^nH^{2n+2}S + P^2O^5$$

2. Alcohols of the form $C^nH^{2n}O = \left.\begin{matrix}C^nH^{2n-1}\\H\end{matrix}\right\}O$ convertible by oxidation into acids of the form $C^nH^{2n-2}O^2$.

Only one term of this series is at present known, viz.: —

Allyl-alcohol or *Hydrate of Allyl*, $C^3H^6O = \left.\begin{matrix}C^3H^5\\H\end{matrix}\right\}O$.

This alcohol was discovered by Cahours and Hofmann in 1856. It is converted by oxidising agents into acrylic aldehyde or acrolein, C^3H^4O, and acrylic acid, $C^3H^4O^2$, and moreover exhibits all the transformations of the bodies of the preceding series (see ALLYL). It is probable that to every acid of the series $C^nH^{2n-2}O^2$ (angelic, terebic, oleic acid, &c), there corresponds an alcohol of the form $C^nH^{2n}O$. These alcohols are isomeric with the aldehydes of the preceding series; *e.g.* allyl-alcohol with propionic aldehyde.

3. Alcohols of the form $C^nH^{2n-2}O = \left.\begin{matrix}C^nH^{2n-3}\\H\end{matrix}\right\}O$. Only one alcohol of this kind is known, viz.:

Camphol, or *Bornean Camphor*, $C^{10}H^{18}O = \left.\begin{matrix}C^{10}H^{17}\\H\end{matrix}\right\}O$. It is a solid substance which, when distilled with anhydrous phosphoric acid, yields the hydrocarbon, $C^{10}H^{16} = C^{10}H^{18}O - H^2O$. It forms neutral ethers with stearic and benzoic acids.

4. Alcohols of the form $C^nH^{2n-6}O = \left.\begin{matrix}C^nH^{2n-7}\\H\end{matrix}\right\}O$, and corresponding to acids of the form $C^nH^{2n-8}O^2$. Three of these alcohols are known, viz.:

Benzyl-alcohol, or *Hydrate of Benzyl*, $C^7H^8O = \left.\begin{matrix}C^7H^7\\H\end{matrix}\right\}O$

Cumyl-alcohol, or *Hydrate of Cumyl*, $C^{10}H^{14}O = \left.\begin{matrix}C^{10}H^{13}\\H\end{matrix}\right\}O$

Sycoceryl-alcohol, or *Hydrate of Sycoceryl*, $C^{18}H^{30}\,O = \left.\begin{matrix}C^{18}H^{29}\\H\end{matrix}\right\}O$

Benzyl-alcohol was discovered by Cannizzaro in 1853; cumyl-alcohol by Kraut in 1854; these two alcohols are obtained by treating the corresponding aldehydes (bitter-almond oil and cuminol) with an alcoholic solution of potash:

$$\underbrace{2C^7H^6O}_{\text{Hydride of benzoyl.}} + KHO = \underbrace{C^7H^8O}_{\text{Benzyl-alcohol.}} + \underbrace{C^7H^5KO^2}_{\text{Benzoate of potassium.}}$$

Moreover, the aldehydes themselves may be formed from acids, by distilling a mixture of the calcium-salt of the acid with formate of calcium, thus:

$$\underbrace{\left.\begin{matrix}C^7H^5O\\Ca\end{matrix}\right\}O}_{\text{Benzoate of calcium.}} + \underbrace{\left.\begin{matrix}CO.H\\Ca\end{matrix}\right\}O}_{\text{Formate of calcium.}} = \underbrace{\left.\begin{matrix}C^7H^5O\\H\end{matrix}\right\}}_{\text{Hydride of of benzoyl.}} + \underbrace{\left.\begin{matrix}CO\\Ca^2\end{matrix}\right\}O^2}_{\text{Carbonate of calcium.}}$$

Hence it appears that these alcohols may be formed from the corresponding acids.

Benzylic and cumylic alcohols are liquids which volatilise without decomposition. They are converted into aldehydes and acids by the action of oxidising agents; they form compound ethers when treated with a mixture of sulphuric acid and other oxygen-acids (*e.g.* acetate of benzyl, $C^2H^3O^2.C^7H^7$, is formed by treating benzyl-alcohol with a mixture of sulphuric and acetic acids), and yield the chlorides of the corresponding radicles when treated with hydrochloric acid; thus chloride of benzyl, C^7H^7Cl is obtained by treating benzyl-alcohol with strong hydrochloric acid.

With sulphuric acid or chloride of zinc, they yield resinous masses, which are probably hydro-carbons analogous to olefiant gas: anhydrous boracic acid converts benzyl-alcohol into benzyl-ether $(C^7H^7)^2O$. They do not appear to form conjugated acids like ethyl-sulphuric acid. By caustic potash, at high temperatures, they are converted into the corresponding acids and hydrides of the alcohol-radicles; *e.g.*:

$$\underbrace{3(C^7H^7.H.O)}_{\text{Benzyl-alcohol.}} = \underbrace{C^7H^6O^2}_{\text{Benzoic acid.}} + \underbrace{2(C^7H^7.H)}_{\text{Hydride of benzyl.}} + H^2O$$

Sycoceryl-alcohol was discovered by Warren De la Rue and Hugo Müller, in 1859 (Proc. Roy. Soc. x. 298). It exists in the form of a natural acetic ether in the exudation from an Australian plant, the *Ficus rubiginosa.* This ether is readily obtained in beautiful crystals, and when treated with sodium-alcohol, yields acetic acid and sycocerylic alcohol, in feathery crystals resembling caffeine or asbestos. Treated with nitric acid, it yields an acid which appears to be sycocerylic acid; and with chromic acid, it yields a product which is probably the corresponding aldehyde.

5. Alcohols isomeric with the last, but differing from them in forming conjugated acids with sulphuric acid, phosphoric acid, &c., and in not being converted into acids and aldehydes by the action of oxidising agents. Two of these alcohols are known, viz.:

Phenyl-alcohol, or *Hydrate of Phenyl,* $C^6H^6O = \left.\begin{matrix}C^6H^5\\H\end{matrix}\right\}O$

Cresyl-alcohol, or *Hydrate of Cresyl,* $C^7H^8O = \left.\begin{matrix}C^7H^7\\H\end{matrix}\right\}O.$

The former was identified as an alcohol by Laurent, in 1841; the latter was discovered by Williamson and Fairlie, in 1854.

Both of these compounds occur among the products of the destructive distillation of coal, and are separated by fractional distillation. Phenyl-alcohol is also produced by the destructive distillation of salicylic acid:

$$C^7H^6O^3 = C^6H^6O + CO^2.$$

Phenyl-alcohol is solid and crystalline at ordinary temperatures, melts at 35°, and distils without decomposition at about 185°. Cresyl-alcohol is liquid at ordinary temperatures.

These alcohols are easily decomposed by potassium and sodium, like common alcohols, hydrogen being evolved, and compounds formed analogous to ethylate of potassium. They exhibit more decided acid characters than any of the preceding alcohols: phenyl-alcohol indeed is sometimes called *phenic* or *carbolic acid:* it forms a series of salts, called phenates or carbolates, containing 1 at. metal in place of the basic hydrogen. These alcohols are not converted into simple ethers or hydrocarbons by heating with sulphuric acid. Strong nitric acid converts them into nitro-acids, *e.g.* phenyl-alcohol into trinitrocarbolic or picric acid, $C^6H^3(NO^2)^3O$.

With pentachloride of phosphorus, they yield a chloride and a phosphate of the radicle together with hydrochloric acid: *e.g.*

$$\underbrace{4(C^6H^5.H.O)}_{\text{Hydrate of phenyl.}} + PCl^2.Cl^3 = \underbrace{PO^4(C^6H^5)^3}_{\text{Phosphate of phenyl.}} + \underbrace{C^6H^5Cl}_{\text{Chloride of phenyl.}} + 4HCl$$

With the chlorides of the acid radicles, they form compound ethers, thus:

$$\underbrace{C^6H^5.H.O}_{\text{Hydrate of phenyl.}} + \underbrace{C^7H^5O.Cl}_{\text{Chloride of benzoyl.}} = \underbrace{C^7H^5O^2.C^6H^5}_{\text{Benzoate of phenyl.}} + HCl$$

6. Alcohols of the form $C^nH^{2n-8}O = \left.\begin{matrix}C^nH^{2n-9}\\ H\end{matrix}\right\}O$. Two only of these bodies are known, viz.:

Cinnamic alcohol, *Hydrate of Cinnamyl*, or *Styrone*, $C^9H^{10}O = \left.\begin{matrix}C^9H^9\\ H\end{matrix}\right\}O$

Cholesterin . . . . . . $C^{26}H^{44}O = \left.\begin{matrix}C^{26}H^{43}\\ H\end{matrix}\right\}O$

Styrone is obtained by heating styracin (cinnamate of cinnamyl), with caustic alkalis; cholesterin is found in the bile and other products of the animal economy. Styrone is converted by oxidising agents into cinnamic aldehyde, C^9H^8O, and cinnamic acid, $C^9H^8O^2$, and forms with fuming sulphuric acid a conjugated acid, the barium-salt of which is soluble in water. Cholesterin heated with strong sulphuric acid gives up water and forms a resinous hydrocarbon, $C^{26}H^{42}$ (Zwenger, Ann. Ch. Pharm. lxv. 5). Heated to 200°, with acetic, butyric, benzoic, and stearic acids, it forms compound ethers, with elimination of water, thus:

$$\underbrace{\left.\begin{matrix}C^{18}H^{35}O\\ H\end{matrix}\right\}O}_{\text{Stearic acid.}} + \underbrace{\left.\begin{matrix}C^{26}H^{43}\\ H\end{matrix}\right\}O}_{\text{Cholesterin.}} = \underbrace{\left.\begin{matrix}C^{18}H^{35}O\\ C^{26}H^{43}\end{matrix}\right\}O}_{\text{Stearate of cholesterin.}} + H^2O$$

7. *Saligenin*, $C^7H^8O^2$, an alcohol of the salicyl-series, and *Anisic alcohol*, $C^8H^{10}O^2$, produced by the action of alcoholic potash on hydride of anisyl, $C^8H^7O^2.H$, are probably monatomic; if so, they must contain oxygen-radicles, their rational formulæ being $\left.\begin{matrix}C^7H^7O\\ H\end{matrix}\right\}O$ and $\left.\begin{matrix}C^8H^9O\\ H\end{matrix}\right\}O$; but they may also be diatomic alcohols, $\left.\begin{matrix}C^7H^6\\ H^2\end{matrix}\right\}O^2$ and $\left.\begin{matrix}C^8H^8\\ H^2\end{matrix}\right\}O^2$. Their reactions are not sufficiently known to decide the question.

B. **Diatomic Alcohols,** or **Glycols.** $C^nH^{2n+2}O^2 = \left.\begin{matrix}(C^nH^{2n})''\\ H^2\end{matrix}\right\}O^2$. These compounds, discovered by Wurtz, are derived from a double molecule of water, $\begin{matrix}H^2\\ H^2\end{matrix}O^2$, in which half the hydrogen is replaced by a diatomic radicle C^nH^{2n}. Four of these have been obtained, viz. *Ethylene-glycol*, or *Hydrate of Ethylene*, $C^2H^6O^2 = \left.\begin{matrix}(C^2H^4)''\\ H^2\end{matrix}\right\}O^2$, *Propylene-glycol*, $C^3H^8O^2$, *Butylene-glycol*, $C^4H^{10}O^2$, and *Amylene-glycol*, $C^5H^{12}O^2$. The simple name *glycol* is especially applied to the first of these, just as the term alcohol is especially applied to hydrate of ethyl, the most important of the monatomic alcohols.

Glycol is obtained by treating iodide of ethylene with acetate of silver, whereby diacetate of ethylene is formed:

$$\underbrace{C^2H^4I^2}_{\text{Iodide of ethylene.}} + \underbrace{\left.\begin{matrix}(C^2H^3O)^2\\ Ag^2\end{matrix}\right\}O^2}_{\text{2 at. acetate of silver.}} = \underbrace{\left.\begin{matrix}C^2H^4\\ (C^2H^3O)^2\end{matrix}\right\}O^2}_{\text{Diacetate of ethylene.}} + 2AgI,$$

and heating the distilled diacetate of ethylene with potash, whereby it is decomposed, like other compound ethers, yielding acetate of potassium and hydrate of ethylene:

$$\left.\begin{matrix}C^2H^4\\ (C^2H^3O^2)^2\end{matrix}\right\}O^2 + 2(KHO) = \left.\begin{matrix}C^2H^4\\ H^2\end{matrix}\right\}O^2 + \left.\begin{matrix}(C^2H^3O)^2\\ K^2\end{matrix}\right\}O^2$$

It was discovered by Wurtz in 1856. The other bodies of the series are obtained by similar processes. They are oily liquids, which distil without decomposition. They contain two atoms of basic hydrogen, one or both of which may be replaced by metals or other radicles.

Glycol treated with sodium yields *monosodic glycol*, $C^2H^4(NaH)O^2$, and this compound, fused with excess of sodium, yields *disodic glycol*, $C^2H^4Na^2O^2$. By treating monosodic glycol with iodide of ethyl, the product with potassium, and this product again with iodide of ethyl, the compounds $C^2H^4(C^2H^5.H)O^2$, $C^2H^4(C^2H^5.K)O^2$, and $C^2H^4(C^2H^5)^2O^2$, are successively obtained. The last is isomeric with acetal, but not identical with it (p. 3), inasmuch as it boils at a temperature 20° below that compound.

Dehydrating agents, such as sulphuric acid and chloride of zinc, do not act upon the glycols in the same manner as upon the corresponding monatomic alcohols. Ethyl-alcohol, $C^2H^5.H.O$, acted upon by sulphuric acid, or chloride of zinc, at certain temperatures, is converted into ether, $(C^2H^5)^2O$, a second atom of ethyl being introduced in place of the remaining hydrogen. If glycol were acted on by these reagents in the same manner, the result would be a glycolic ether containing $(C^2H^4)^2O^2$. Instead of this, the change which takes place is a simple abstraction of water, and the resulting compound is *aldehyde*, C^2H^4O, a body of isomeric composition, but only half the atomic weight:

$$C^2H^6O^2 - H^2O = C^2H^4O.$$

Similar results are obtained with the other glycols. The aldehydes are isomeric with the ethers of the diatomic alcohols (see ETHERS, and ETHYLENE, OXIDE OF); and their mode of formation from these alcohols differs from the etherification of the monatomic alcohols in the same manner as the conversion of dibasic acids into anhydrides differs from that of monobasic acids,—the latter being converted into anhydrides by duplication of the radicle: *e. g.* acetic acid = $C^2H^3O.H.O$; acetic anhydride = $(C^2H^3O)^2O$, whereas dibasic acids pass to the state of anhydrides by simple abstraction of water, *e. g.* $SO^4H^2 - H^2O = SO^3$. (Wurtz, Compt. rend. xlvii. 346.)

By treating diatomic alcohols, first with hydrochloric acid and afterwards with potash, compounds are obtained isomeric with the aldehydes, and resembling them in some of their properties, but differing in others; thus, ethylene-glycol, heated in a sealed tube with hydrochloric acid, yields *monochlorhydric glycol*, C^2H^5ClO, a compound intermediate between glycol and chloride of ethylene, $C^2H^4Cl^2$, and formed from glycol by the substitution of Cl for 1 atom of peroxide of hydrogen:

$$C^2H^4.H^2O^2 + HCl = C^2H^4.HO.Cl + H^2O;$$

and this compound, treated with potash, yields oxide of ethylene, a body isomeric with acetic aldehyde:

$$C^2H^4.HO.Cl + KHO = C^2H^4O + H^2O + KCl.$$

This oxide of ethylene resembles aldehyde in being miscible with water, and in forming a crystalline compound with acid sulphite of sodium; but differs from it by boiling at a lower temperature, and by not forming a crystalline compound with ammonia. Similar results are obtained with propylene-glycol. (Wurtz, Compt. rend. xlviii. 100.)

The glycols corresponding to the other series of monatomic alcohols, have not yet been obtained; but several diatomic compound ethers containing benzylene, C^7H^6, have been produced, viz. the acetate, valerate, and benzoate, $C^7H^6.(C^2H^3O)^2.O^2$, &c.; the methylate, ethylate, and amylate, $C^7H^6.(CH^3)^2.O^2$, &c.; the sulphate, $SO^4.C^7H^6$, and the succinate, $C^7H^6.C^4H^4O^2.O^2$. The diatomic alcohol, $C^7H^6.H^2O^2$, corresponding to those compound ethers, has not yet been obtained, not being produced when the ethers are decomposed by alkalis. (W. Wicke, Ann. Ch. Pharm. cii. 363.)

C. **Triatomic Alcohols, or Glycerins.** The general formula of these compounds is $\left.\begin{matrix}C^nH^{2n-1}\\H^3\end{matrix}\right\}O^3$, the radicle C^nH^{2n-1} being equivalent to three atoms of hydrogen. One term of the series has long been known, viz. ordinary glycerin, $C^3H^8O^3 = \left.\begin{matrix}C^3H^5\\H^3\end{matrix}\right\}O^3$, the sweet oily liquid obtained in the saponification of fats. It was first shown to be a triatomic alcohol by Berthelot, in 1853. (Compt. rend. xxxvii. 398.)

The neutral fats of the animal body, stearin, palmitin, olein, &c., consist of glycerin, in which three atoms of hydrogen are replaced by acid radicles; and by heating glycerin with acids in different proportions, a large number of compounds may be formed, in which $\frac{1}{3}$, $\frac{2}{3}$, or the whole of the replaceable hydrogen is thus replaced, the formation of these compounds being accompanied by the elimination of 1, 2, or 3 atoms of water. Thus, with stearic acid, $C^{18}H^{36}O^2$, the following compounds are obtained:

Monostearin $= C^{21}H^{42}O^4 = C^3H^8O^3 + C^{18}H^{36}O^2 - H^2O = \left.\begin{matrix}(C^3H^5)'''\\H^2.C^{18}H^{35}O\end{matrix}\right\}O^3.$

Distearin $= C^{39}H^{76}O^5 = C^3H^8O^3 + 2C^{18}H^{36}O^2 - 2H^2O = \left.\begin{matrix}(C^3H^5)'''\\H.(C^{18}H^{35}O)^2\end{matrix}\right\}O^3$

Tristearin (natural stearin) $= C^{57}H^{110}O^6 = C^3H^8O^3 + 3C^{18}H^{36}O^2 - 3H^2O = \left.\begin{matrix}(C^3H^5)'''\\(C^{18}H^{35}O)^3\end{matrix}\right\}O^3.$

Precisely similar actions take place on heating glycerin with hydrochloric, hydrobromic, or hydriodic acid; but to refer the resulting compounds to the same type, it is best to write the formula of glycerin thus: $C^3H^5(HO)^3$, representing it as a compound of glyceryl with 3 at. peroxide of hydrogen: then the compounds just mentioned may be represented as glycerin in which 1, 2, or 3 at. peroxide of hydrogen are replaced by Cl, Br, I, &c. Thus:

Monochlorhydrin $= C^3H^7ClO^2 = C^3H^8O^3 + HCl - H^2O = C^3H^5Cl(HO)^2$
Dichlorhydrin $= C^3H^6Cl^2O = C^3H^8O^3 + 2HCl - 2H^2O = C^3H^5Cl^2(HO)$
Trichlorhydrin $= C^3H^5Cl^3 = C^3H^8O^3 + 3HCl - 3H^2O$
Bromhydrodichlorhydrin $= C^3H^5Cl^2Br = C^3H^8O^3 + 2HCl + HBr - 3H^2O$.

The chlorhydrins and bromhydrins are likewise produced by treating glycerin with either of the bromides or chlorides of phosphorus. (See GLYCERIN.)

By treating glycerin with the chloride of an acid radicle, or by passing hydrochloric acid gas into a solution of glycerin in the corresponding acid, compounds are formed which may be regarded as glycerin, in which the peroxide of hydrogen is replaced partly by chlorine and partly by the peroxide of the acid radicle; thus with acetic acid [$Ac = C^2H^3O$]:

Acetochlorhydrin $= C^5H^9ClO^3 = C^3H^8O^3 + C^2H^4O^2 + HCl - 2H^2O = C^3H^5.Cl(AcO)(HO)$.
Diacetochlorhydrin $= C^7H^{11}ClO^4 = C^3H^8O^3 + 2C^2H^4O^2 + HCl - 3H^2O = C^3H^5.Cl(AcO)^2$
Acetodichlorhydrin $= C^5H^6Cl^2O^2 = C^3H^8O^3 + C^2H^4O^2 + 2HCl - 3H^2O = C^3H^5.Cl^2AcO$.

(For further details, see ACETINS, p. 25.)

All these compounds, when heated with caustic alkalis, or with metallic oxides and water, reproduce the acid and the glycerin; thus stearin heated with caustic potash, yields glycerin and stearate of potassium:

$$\left.\begin{matrix}C^3H^5\\(C^{18}H^{35}O)^3\end{matrix}\right\}O^3 + 3KHO = \left.\begin{matrix}C^3H^5\\H^3\end{matrix}\right\}O^3 + 3\left(\left.\begin{matrix}C^{18}H^{35}O\\K\end{matrix}\right\}O\right)$$

Glycerin may also be formed synthetically in a similar manner to glycol, viz. by heating tribromhydrin, $C^3H^5Br^3$, with acetate of silver, whereby triacetin, $C^3H^5Ac^3O^3$ is formed, and heating this compound with solution of caustic baryta. The other glycerins have not yet been obtained in the free state, but the *acetate of ethyl-glycerin* $(C^2H^3)'''Ac^3O^3$ appears to be obtained, together with glycol, by the action of iodide of ethylene on acetate of silver.

D. **Alcohols not included in any of the preceding groups.**—Berthelot has shown that a considerable number of substances, not usually classed as alcohols, nevertheless possess one essential character of those bodies, viz. that they unite with acids, producing neutral compounds, the formation of which is attended with elimination of water; and these compounds, when heated with alkalis, reproduce the substances from which they have been formed. The bodies in question are chiefly of a saccharine nature, viz. *Mannite*, $C^6H^{12}O^5.H^2O$, the sugar of manna; *Dulcin*, $C^6H^{12}O^5.H^2O$, a saccharine substance from an unknown plant, brought from Madagascar; *Pinite*, $C^6H^{12}O^5$, a sugar from the *Pinus lambertiana*, a tree growing in California; *Quercite*, $C^6H^{12}O^5$, the sugar of acorns; *Erythromannite*, *Erythroglucin*, or *Phycite*, $C^6H^{14}O^6$, a sugar obtained from certain lichens, and from the *Protococcus vulgaris*.—*Orcin*, $C^7H^8O^2$, a sweet crystalline substance, existing in the lichens which yield archil and litmus; *Trehalose*, $C^6H^{10}O^5$, also a kind of sugar; *Glucose*, $C^6H^{12}O^6$, and *Meconin*, $C^{10}H^{10}O^4$, an acrid crystallisable substance, obtained from opium. The following are examples of the compounds formed:

$$\underset{\text{Mannitan.}}{C^6H^{12}O^5} + \underset{\text{Acetic acid.}}{2C^2H^4O^2} - 2H^2O = C^{10}H^{16}O^7$$

$$\underset{\text{Mannitan.}}{C^6H^{12}O^5} + \underset{\text{Stearic acid.}}{4C^{18}H^{36}O^2} - 2H^2O = C^{78}H^{152}O^{11}$$

$$\underset{\text{Mannitan.}}{C^6H^{12}O^5} + \underset{\text{Stearic acid.}}{6C^{18}H^{36}O^2} - 6H^2O = C^{114}H^{216}O^{11}$$

$$\underset{\text{Phycite.}}{C^6H^{14}O^6} + \underset{\text{Benzoic acid.}}{2C^7H^6O^2} - 2H^2O = C^{20}H^{22}O^8 \quad (?)$$

$$\underset{\text{Phycite.}}{C^6H^{14}O^6} + \underset{\text{Benzoic acid.}}{6C^7H^6O^2} - 6H^2O = C^{48}H^{38}O^{12} \quad (?)$$

$$\underset{\text{Glucose.}}{C^6H^{12}O^6} + \underset{\text{Stearic acid.}}{2C^{18}H^{36}O^2} - 3H^2O = C^{42}H^{78}O^7$$

$$\underset{\text{Meconin.}}{C^{10}H^{10}O^4} + \underset{\text{Stearic acid.}}{2C^{18}H^{36}O^2} - 2H^2O = C^{46}H^{78}O^6.$$

The compounds formed by all these bodies, excepting the last two, with acids, readily yield the original saccharine substance and the acid. The compounds formed with glucose are not very definite, and not easily decomposed; but when treated with dilute sulphuric acid, they yield the original acid and a fermentable sugar, which reduces copper salts. (Berthelot, Compt. rend. xli. 452; xlvii. 262.)

ALDEHYDE. $C^2H^4O = C^2H^3O.H.$ [or $C^4H^4O^2 = C^4H^3O.HO$]. *Acetic aldehyde, Hydride of Acetyl* (Gm. viii. 274; xiii. 437; Gerh. i. 658).—A volatile liquid produced by the oxidation and destructive distillation of alcohol and other organic compounds. It was first obtained in an impure state by Döbereiner, who called it *Light oxygen ether*, and was afterwards prepared pure and thoroughly examined by Liebig (Ann. Ch. Pharm. xiv. 133; xxxvi. 376). The name *aldehyde* is an abbreviation of *alcohol dehydrogenatum*, inasmuch as the compound may be regarded as alcohol deprived of two atoms of hydrogen.

Formation.—1. In the oxidation of alcohol, either by slow combustion in contact with platinum-black, chromic oxide, &c., or by the action of chromic acid, nitric acid, chlorine water, or a mixture of sulphuric acid and peroxide of manganese (see ALCOHOL, p. 74).—2. When the vapour of alcohol or ether is passed through a tube heated to dull redness; also in the slow combustion of ether.—3. In the decomposition of acetate of ethyl, and probably also of other ethylic ethers, by a mixture of sulphuric acid and acid chromate of potassium.—4. By heating acetal with glacial acetic acid to between 150° and 200° C. for two days. Acetic ether and alcohol are formed at the same time, and on distilling the mixture, aldehyde passes over below 60°:

$$\underbrace{C^6H^{14}O^2}_{\text{Acetal.}} + \underbrace{C^2H^4O^2}_{\text{Acetic acid.}} = \underbrace{C^2H^4O}_{\text{Aldehyde.}} + \underbrace{C^4H^8O^2}_{\text{Acetic ether.}} + \underbrace{C^2H^6O}_{\text{Alcohol.}}$$

also by heating acetal with acetic anhydride:

$$C^6H^{14}O^2 + C^4H^6O^3 = C^2H^4O + 2C^4H^8O^2.$$

A few drops of liquid are also obtained boiling above 150°, and probably consisting of a compound of aldehyde with acetic anhydride (Beilstein, Compt. rend. xlviii. 1121).—5. By heating ethyl-sulphuric acid or one of its salts with a mixture of sulphuric acid and peroxide of manganese. This formation of aldehyde is said to take place under circumstances which altogether preclude any previous formation of alcohol (Jacquemin and Liès-Bodard, l'Institut, 1857, p. 407).—6. When hemp-oil is passed through a gun-barrel heated to low redness, a liquid is formed containing a large quantity of aldehyde, together with alhehydic or lampic acid (Hess).—7. By the dry distillation of lactic acid, lactic anhydride, and lactates with weak bases, such as lactate of copper, carbonic oxide being given off at the same time:

$$\underbrace{C^6H^{12}O^6}_{\text{Lactic acid.}} = \underbrace{2C^2H^4O}_{\text{Aldehyde.}} + 2CO + 2H^2O.$$

8. Lactic acid and the lactates also yield considerable quantities of aldehyde when distilled with sulphuric acid and peroxide of manganese (Städeler, Ann. Ch. Pharm. lxxix. 333).—9. In the decomposition of animal albumin, fibrin, casein, and gelatin by a mixture of sulphuric acid and peroxide of manganese, or bichromate of potassium (Guckelberger), also of vegetable fibrin by sulphuric acid and peroxide of manganese (Keller).—10. By the dry distillation of a mixture of acetate and formate of calcium in equal numbers of atoms (Limpricht. See ALDEHYDES, p. 111; also ACETONES, p. 31).

$$\underbrace{C^2H^3CaO^2}_{\text{Acetate of calcium.}} + \underbrace{CHCaO^2}_{\text{Formate of calcium.}} = \underbrace{C^2H^4O}_{\text{Aldehyde.}} + \underbrace{CO^3Ca^2}_{\text{Carbonate of calcium.}}.$$

Preparation.—1. Two pts. of 80 per cent. alcohol are mixed with 3 pts. peroxide of manganese, 3 pts. oil of vitriol and 2 pts. water, and distilled into a receiver kept at a very low temperature. The mixture is gently heated till it begins to froth slightly, and the distillation is interrupted as soon as the liquid which passes over begins to redden litmus, which it does when the distillate amounts to 3 pts. The distillate, consisting of aldehyde, alcohol, &c., is mixed with an equal weight of chloride of calcium, and distilled (the receiver being constantly kept very cold), till 1½ pt. has passed over, and this distillate is again rectified with an equal weight of chloride of calcium till ¾ pt. has passed over. This last portion is anhydrous, but contains alcohol and certain compound ethers as well as aldehyde. To purify it, 1 vol. is mixed with 2 vol. ether, the mixture surrounded with cold water, and dry ammoniacal gas passed into it to saturation; the gas is absorbed rapidly and with great evolution of heat, and the aldehyde separates out in crystals of aldehyde-ammonia. These crystals are washed three times with absolute ether and dried as above. (Liebig.)

2. A mixture of 1 pt. 80 per cent. alcohol and 2 pts. water is saturated with chlorine gas (being kept cool all the while), and the liquid distilled, as soon as it has lost the odour of chlorine, till $\frac{1}{20}$ has passed over. That which distils over afterwards is alcohol, which may be collected in a separate receiver and again treated with chlorine as above. The first distillate is again freed from water by repeated distillation so far as to admit of its being saturated with ammonia as above, and yields a very large crop of crystals. (Liebig.)

3. One part of alcohol of sp. gr. 0·842 and 1 pt. of bichromate of potassium are introduced into a capacious tubulated retort and 1⅓ pt. oil of vitriol admitted by drops through the tubulus. The heat evolved by the chemical action which ensues is sufficient to begin the distillation, but towards the end, heat must be applied from without. A large quantity of carbonic acid gas is evolved, and the aldehyde condenses in the well cooled receiver, contaminated with only a small quantity of acetic acid and other substances, so that the distillate may be immediately mixed with ether, and ammoniacal gas passed through it as above (W. and R. Rodgers, J. pr. Chem. xl. 248). The modes of formation 5, 6, and 8, above given, may also be advantageously used for the preparation of aldehyde.

To obtain the pure anhydrous aldehyde from the aldehyde-ammonia formed by either of these processes, a solution of 2 pts. of the aldehyde-ammonia in 2 pts. water, is distilled in a water-bath at a gentle but increasing heat, with a mixture of 3 pts. sulphuric acid and 4 pts. water, the distillation being interrupted as soon as the water in the bath begins to boil, and the receiver kept as cold as possible. The hydrated aldehyde which passes over is dried by contact with coarse lumps of chloride of calcium in a well closed vessel, and then rectified in a water-bath, at a temperature not exceeding 30°.

Properties.—Aldehyde is a thin, transparent, colourless liquid, having a pungent suffocating odour. Its specific gravity is 0·80002 at 0° (Kopp); 0·80551 at 0° (Pierre). It boils at 20·8° when the barometer stands at 760 mm. (Kopp); at 22°, with the barometer at 758·2 mm (Pierre). Vapour-density 1·532 (Liebig); (by calculation, 1·520, for a condensation to 2 vol.) It does not redden litmus, even when it is dissolved in water or alcohol.

Aldehyde may be regarded either as the *hydride of acetyl*, $C^2H^3O.H$, or as the *hydrate* or *hydrated oxide of vinyl*,  $\left.\begin{matrix}C^2H^3\\H\end{matrix}\right\}O$. Its chemical reactions may for the most part be explained equally well on either hypothesis; but according to the recent observations and calculations of Kopp, the formula $C^2H^3O.H$, is most in accordance with the observed atomic volume of aldehyde, which is between 56·0 and 56·9, the calculated atomic volume being 56·2, as deduced from the first formula, and 51·8 as deduced from the second. (See ATOMIC VOLUME: also Graham's Chemistry, 2nd Ed. vol. ii. p. 581.)—Aldehyde is isomeric, but not identical, with the oxide of ethylene, $C^2H^4.O$, recently discovered by Wurtz.

Aldehyde mixes in all proportions with *water*, *alcohol*, and *ether*. A mixture of 1 pt. aldehyde and 3 pts. water boils at 37°. Chloride of calcium added to the aqueous solution separates the aldehyde, which then rises to the surface.

Aldehyde dissolves *sulphur* and *phosphorus*, also *iodine*, forming a brown solution.

Dry sulphurous acid gas passed into anhydrous aldehyde surrounded with cold water, is rapidly absorbed, 11 pts. of aldehyde absorbing 9 pts. of the gas, with increase of volume. The absorption-coefficient of aldehyde for sulphurous acid gas is 1·4 times as great as for alcohol, and 7 times as great as for water. (Geuther and Cartmell, Ann. Ch. Pharm. cxi. 17.)

Decompositions.—1. Aldehyde is very inflammable, and burns with a blue flame.—2. When kept in close vessels, it is often converted into a less volatile liquid, or into two crystalline bodies, which are isomeric modifications of aldehyde (p. 109).—3. In vessels containing *air*, it absorbs oxygen, and is converted into acetic acid; the action is greatly accelerated by the presence of platinum black.—4. *Chlorine-water* and *nitric acid* also convert aldehyde into acetic acid.—5. By strong *sulphuric acid*, it is thickened and blackened, also by *phosphoric anhydride*.—6. When an aqueous or alcoholic solution of aldehyde is heated with *potash*, it becomes yellowish and turbid, and a red-brown resinous mass, the *resin of aldehyde*, separates on the surface, the liquid at the same time emitting a spirituous and disagreeably pungent odour. The solution is afterwards found to contain formate and acetate of potassium. This is the most characteristic reaction of aldehyde.—7. When vapour of aldehyde is passed over red-hot *potash-lime*, acetate of potassium is formed and hydrogen evolved:

$$C^2H^4O + KHO = C^2H^3KO^2 + 2H.$$

8. *Potassium* (or *sodium*) acts on aldehyde in the same manner as on alcohol, hydrogen being evolved and aldehydate of potassium, C^2H^3KO, produced.—9. When an

aqueous solution of aldehyde is heated with *oxide* or *nitrate of silver*, mixed with a small quantity of *ammonia*, the silver is reduced, forming a beautiful specular coating on the side of the vessel, and acetate of silver is formed in the solution. This reaction affords an extremely delicate test for aldehyde.—10. *Chlorine gas* in contact with aldehyde, both being dry, decomposes part of the aldehyde, forming chloride of acetyl, which then unites with the undecomposed aldehyde, forming the compound, $C^2H^4O.C^2H^3OCl$.—11. When dry *hydrochloric acid gas* is passed into anhydrous aldehyde surrounded by a freezing mixture, the gas is absorbed, and the liquid separates into two layers, the lower consisting of water saturated with hydrochloric acid, and the upper of *oxychloride of ethylidene*, $C^4H^8Cl^2O$ (A. Lieben, Compt. rend. xlvi. 662):

$$2C^2H^4O + 2HCl = C^4H^8Cl^2O + H^2O.$$

According to Geuther and Cartmell (Ann. Ch. Pharm. cxii. 13; Proc. Roy. Soc. x. 110) the first product of the action is the body, $C^6H^{12}Cl^2O^2$, which, when gently heated in an atmosphere of carbonic acid, splits up into aldehyde, C^2H^4O, and $C^4H^8Cl^2O$. The compound $C^6H^{12}Cl^2O^2$, may be regarded as a triple molecule of aldehyde ($C^6H^{12}O^3$), having one atom O replaced by Cl^2.—12. Aldehyde mixed with twice its bulk of absolute alcohol, and saturated in the cold with hydrochloric acid gas, yields the compound C^4H^9ClO, which, when treated with ethylate of sodium, forms acetal (p. 3).—13. With *pentachloride of phosphorus*, aldehyde yields chloride of ethylidene, $C^2H^4Cl^2$, and with *pentabromide of phosphorus* it yields bromide of ethylidene, $C^2H^4Br^2$, which is converted by ethylate of sodium into acetal (p. 4).—14. *Chlorocarbonic oxide* (phosgene gas) converts aldehyde into chloride of vinyl, C^2H^3Cl, with evolution of hydrochloric acid and carbonic anhydride. (Harnitz Harnitzky, Ann. Ch. Pharm. cxi. 192.)

$$C^2H^4O + COCl^2 = C^2H^3Cl + HCl + CO^2.$$

15. *Hydriodic acid* gas appears to act upon aldehyde in the same manner as hydrochloric acid, but the product is very unstable.—16. When aqueous aldehyde is saturated with *hydrosulphuric acid gas*, a viscid oil is formed, consisting of *hydrosulphate of acetyl-mercaptan:* $C^{12}H^{26}S^7 = SH^2.6C^2H^4S$. On treating this oil with strong hydrochloric or sulphuric acid, hydrosulphuric acid escapes, and a white crystalline mass remains, consisting of *acetyl-mercaptan*, C^2H^4S, a compound related to aldehyde, in the same manner as ethyl-mercaptan, C^2H^6S, to alcohol.—17. *Cyanic acid* vapour evolved from cyanuric acid is quietly absorbed by anhydrous aldehyde at 0°; but even at ordinary temperatures the mixture becomes heated, gives off carbonic anhydride, and ultimately froths up and solidifies into a mass consisting of *trigenic acid*, $C^4H^7N^3O^2$, together with small quantities of cyamelide, aldehyde-ammonia, and other products (Liebig and Wohler):

$$C^2H^4O + 3CNHO = C^4H^7N^3O^2 + CO^2.$$

ALDEHYDATES.—Aldehyde may be regarded as a monobasic acid, inasmuch as it contains one atom of hydrogen replaceable by metals. Thus, when potassium is gently heated with aldehyde, hydrogen is evolved, and aldehydate of potassium, C^2H^3KO, produced: and by evaporation in vacuo this salt may be obtained in the solid state.—Aldehydate of silver, C^2H^3AgO, is produced when oxide of silver is heated with aldehyde and ammonia. The most important of these salts is the ammonium-salt:

Aldehydate of Ammonium, Aldehyde-ammonia, Acetyl-ammonium, $C^2H^4O.NH^3 = C^2H^3O.NH^4$, or *Oxide of Vinyl and Ammonium*, $C^2H^3.NH^4.O$.—Ammoniacal gas passed into pure aldehyde combines with it, giving off heat, and forming a white crystalline mass. If the aldehyde be previously mixed with ether, the compound separates in distinct crystals; the finest are obtained by mixing a concentrated alcoholic solution of aldehyde-ammonia with ether (Liebig).—The crystals are acute rhombohedrons with terminal edges of about 85°, often truncated with the faces of another rhombohedron (G. Rose); they are transparent, colourless, shining, strongly refractive, of the hardness of common sugar, and very friable. The compound melts between 70° and 80° C., and distils unaltered at 100°. In the state of vapour or in aqueous solution, it reddens turmeric paper. Its odour is ammoniacal, but has likewise the character of turpentine (Liebig).—It dissolves very easily in water, less easily in alcohol and ether.

Aldehyde-ammonia is very inflammable. In contact with the air, especially if also exposed to light, it becomes yellow, and acquires an odour resembling that of burnt animal substances. By distillation it may again be obtained in the colourless state, and leaves a brown residue, which is soluble in water, and contains acetate of ammonium and another ammoniacal salt. Even the weaker acids, such as acetic acid, separate the aldehyde from the compound. Sulphuric acid and potash act upon it in the same manner as upon aldehyde. Its aqueous solution, digested with oxide of silver, reduces part of this oxide and dissolves the rest, forming aldehydate and acetate of silver mixed with ammonia, from which the oxide of silver is precipitated by baryta-water, and reduced when the liquid is heated, while acetate of barium remains in solution.

Aldehyde-ammonia treated with hydrosulphuric acid yields *thialdine*, $C^6H^{13}NS^2$:

$$3(C^2H^3O.NH^4) + 3H^2S = C^6H^{13}NS^2 + (NH^4)^2S + 3H^2O.$$

Similarly, with hydroselenic acid, it yields *selenaldine*, $C^6H^{13}NSe^2$. With bisulphide of carbon it forms *carbothialdine*:

$$\underbrace{2(C^2H^3O.NH^4)}_{\text{Aldehyde-ammonia.}} + CS^2 = \underbrace{C^5H^{10}N^2S^2}_{\text{Carbothialdine.}} + 2H^2O$$

Aldehyde-ammonia heated with hydrocyanic and hydrochloric acids yields *alanine:*

$$\underbrace{C^2H^4O.NH^3}_{\text{Aldehyde-ammonia.}} + \underbrace{CNH}_{\text{Hydrocyanic acid.}} + H^2O + HCl = \underbrace{C^3H^7NO^2}_{\text{Alanine.}} + NH^4Cl.$$

But when a mixture of aldehyde-ammonia and hydrocyanic acid, with sufficient hydrochloric acid to give it a distinct acid reaction, is left to itself for some time, in a closed vessel, especially in sunshine, colourless needle-shaped crystals are formed, consisting of *hydrocyanaldine*, $C^9H^{12}N^4$:

$$3(C^2H^4O.NH^3) + 3CNH + 2HCl = C^9H^{12}N^4 + 2NH^4Cl + 3H^2O.$$

Aldehyde-ammonia heated in a sealed tube to 120° C. is decomposed, and yields two layers of liquid, the upper consisting chiefly of aqueous ammonia, with small quantities of other volatile bases, while the lower, which remains behind on distilling at 200°, contains a substance which has the composition $C^{10}H^{15}NO$, and may be regarded as an *aldehydate of tetravinylium:* $=C^2H^3O.N(C^2H^3)^4$. Its formation is represented by the equation:

$$5(C^2H^3O.NH^4) = C^{10}H^{15}NO + 4NH^3 + 4H^2O.$$

By treating this compound with baryta-water, the group C^2H^3O is replaced by HO. and *hydrate of tetravinylium* is formed.

$$C\,H^3O.N(C^2H^3)^4 + BaHO = C^2H^3O.Ba + N(C^2H^3)^4.H.O.$$

(Babo, J. pr. Chem. lxxii. 88; Chem. Gaz. 1858, 136.)

Concentrated aqueous solutions of aldehyde-ammonia and nitrate of silver yield, when mixed, a fine-grained white precipitate, probably consisting of $NO^3Ag.2(C^2H^3O.NH^4)$. It dissolves very sparingly in alcohol, easily in water.

Sulphite of Aldehyde-ammonia, or *Sulphite of Vinyl-ammonium*, $C^2H^3(NH^4)O.SO^2 = (C^2H^3.NH^4).SO^3$.—Sulphurous acid gas passed into a solution of aldehyde-ammonia in absolute alcohol is rapidly absorbed; and if the liquid be kept cool, sulphite of aldehyde-ammonia is deposited in small white prisms, which may be washed with alcohol and dried in vacuo. This compound is isomeric with taurin, $C^2H^7NO^3S$—a substance produced by the metamorphosis of a sulphur-acid contained in the bile—but possesses very different properties. It is soluble in water and in aqueous alcohol, very sparingly in absolute alcohol. The crystals decompose slowly in the air at ordinary temperatures, turn brown and lose weight at 100°, and are completely decomposed at higher temperatures, leaving a spongy carbonaceous residue. Acids decompose them, liberating aldehyde and sulphurous anhydride. When strongly heated with potash-lime, they give off ethylamine (Gössmann, Ann. Ch. Pharm. xci. 122), or rather perhaps dimethylamine:

$$C^2H^3.NH^4.SO^3 + KHO = C^2H^7N + SO^4.HK.$$

COMPOUND OF ALDEHYDE WITH ACETIC ANHYDRIDE, $C^6H^{10}O^4 = C^4H^6O^3.C^2H^4O$.—When 1 at. acetic anhydride and 1 at. pure aldehyde are heated together in a sealed tube to 180° C. for about 12 hours, they unite and form a liquid compound which may be freed from unaltered aldehyde and acetic anhydride by fractional distillation, further purified by washing the portion which passes over above 140° with hot water, and dehydrated over chloride of calcium. It then boils at 168°. It has an alliaceous odour and slight acid reaction, probably arising from decomposition during distillation. Heated with hydrate of potassium, it yields acetate of potassium, giving off the peculiar odour of aldehyde when similarly treated. This reaction distinguishes the compound from Wurtz's acetate of ethylene (acetate of glycol), $C^2H^4(C^2H^3O)^2.O^2$ with which it is isomeric: for that compound heated with caustic alkalis, yields hydrate of ethylene (glycol), without any odour of aldehyde. (Geuther, Ann. Ch. Pharm. cvi. 249.)

Aldehyde appears to form similar compounds with *benzoic* and *succinic anhydrides*.

Compound of Aldehyde with Chloride of Acetyl, $C^4H^7ClO^2 = C^2H^4O.C^2H^3OCl$. —Chloride of acetyl and aldehyde heated together to 100° for three hours in a sealed tube, unite and form a liquid which distils completely between 90° and 140° C. and yields by fractional distillation a considerable quantity of liquid, boiling between 120° and 124°. This liquid is lighter than water; is very slowly decomposed by cold water, more quickly by hot water; and dissolves easily in dilute potash, forming chloride and acetate of potassium, and yielding free aldehyde which is partly resinised by the potash. Moist oxide of silver also decomposes it, forming chloride and acetate of silver. (Maxwell Simpson, Compt.-rend. xlvii. 174.)

The same compound is produced, according to Wurtz (Ann. Ch. Phys. [3] xliv. 58), together with chloride of acetyl, by introducing perfectly dry aldehyde into a large vessel filled with dry chlorine. Its formation is due to the union of the chloride of acetyl first produced with the remaining aldehyde (compare p. 106). Wurtz, however, regards it as a double molecule of aldehyde ($C^4H^8O^2$), having 1 at. H replaced by chlorine.

Modifications of Aldehyde.—Aldehyde is susceptible of four isomeric modifications, two liquid and two solid.

a. Liquid modifications.—1. Pure aldehyde sealed up in a tube changes in the course of a few weeks into a liquid, which has a pleasant ethereal odour, boils at about 81°, and no longer forms a resin with potash; it may be exposed to the air without oxidising, and floats on water without mixing. (Liebig)

2. Pure aldehyde mixed with about half its bulk of water and a trace of sulphuric or nitric acid, and cooled to 0° C., changes into a liquid which is no longer miscible with water, and after being purified by agitation with water, and rectification over chloride of calcium, boils at 125°. It has a peculiar aromatic burning taste, and is soluble in alcohol and ether, sparingly also in water. Its vapour-density is 4·583, which for a condensation to 2 volumes, corresponds to the formula $C^6H^{12}O^3$. When left to itself, or in contact with water, it readily changes into an acid, and then becomes miscible with water; occasionally also crystals separate from it at the same time. When heated with a small quantity of sulphuric or nitric acid, it is converted into ordinary aldehyde. (Weidenbusch, Ann. Ch. Pharm. lxvi. 155.)

b. Solid modifications.—1. *Solid and fusible Elaldehyde.*—Anhydrous aldehyde, enclosed in a tube, together with pieces of chloride of calcium, for two months in winter, yielded long transparent prisms, which, however, disappeared again after a fortnight, so completely that not a trace of them could be perceived in the liquid.—These crystals melt at + 2° C., forming a liquid which solidifies at 0°, and boils at 94°, giving off a vapour whose density is 4·5157. In the fused state, this substance has an ethereal odour; more agreeable and less pungent than that of aldehyde; its taste is somewhat burning. Its burns with a blue flame; its vapour passed through a red-hot tube yields a combustible gaseous mixture, and a small quantity of a liquid having an empyreumatic odour. Oil of vitriol blackens the crystals slowly in the cold, immediately when heated. The crystals may be heated with potash-ley for some time without becoming coloured, and solidify again on the surface as the liquid cools. When heated with aqueous nitrate of silver, they throw down the silver in the form of a grey powder, not as a specular coating. When dissolved in ether, they do not absorb ammoniacal gas but remain unaltered. (Fehling, Ann. Ch. Pharm. xxvii. 319.)

Geuther and Cartmell (Ann. Ch. Pharm. cxi. 16) have obtained a similar modition, by saturating common aldehyde with sulphurous acid gas, dissolving the resulting liquid in water, saturating the acid with chalk, distilling, and treating the distillate with potash, which separates the remaining common aldehyde in the resinous form, and leaves the modified aldehyde in the form of a clear liquid, which boils at 124° C., like the modification obtained by Weidenbusch, and solidifies at 10°, starting into crystals which also begin to melt at 10°.

2. *Solid and infusible Metaldehyde.*—Anhydrous aldehyde kept for some time in a sealed tube or well stoppered bottle, frequently deposits transparent, colourless, four-sided prisms, which traverse the whole liquid like a network. The crystals remain solid at 100° C., but at a stronger heat sublime undecomposed, in the form of transparent, colourless, shining, rather hard needles, which are easily pulverised, inodorous, combustible, scarcely at all soluble in water, but easily soluble in alcohol and ether (Liebig).—Fehling, by exposing pure aldehyde to the cold of winter for several weeks, once obtained the same crystals, mixed, however, with a larger quantity of the crystals *b*. They are hard and easy to pulverise; at 120° they sublime without previous fusion. When they are suffered to evaporate in the air, the vapour condenses in fine snowy flakes (Liebig). Heated for some time to 180° in sealed tubes they are reconverted into ordinary aldehyde. (Geuther, Ann. Ch. Pharm. cvi. 252.)

Aldehyde-resin.—A resinous body obtained by heating aldehyde with potash, either in aqueous or in alcoholic solution, especially the latter. It is also formed in solutions of the alkalis in alcohol, and in acetal, when kept for a long time. According to Weidenbusch (Ann. Ch. Pharm. lxvi. 153) it is a substance of a fiery orange colour which is reduced by drying at 100°, to a powder, having a paler tint. It dissolves in alcohol and ether, sparingly in water, scarcely at all in alkalis, partially in strong sulphuric acid, from which it is precipitated by water. When purified as completely as possible, it contains 76·4 per cent. of carbon, and 8·0 per cent. of hydrogen: its formation is accompanied by that of acetic, formic and acetylous [?] acid; at the same time a pungent odour is evolved, proceeding from a peculiar substance which adheres obstinately to the resin. This substance is oily and volatile when first produced, but soon thickens, even when alone and still more quickly under the influence of nitric acid, and is converted into a golden-yellow, viscid resin, which smells like cinnamon, dissolves in alcohol and ether, and sparingly in water, and is different from the true aldehyde-resin.

ALDEHYDES. A class of organic compounds intermediate between alcohols and acids. They are derived from alcohols by abstraction of 2 atoms of hydrogen, and are converted into acids by addition of 1 atom of oxygen: thus in the fatty acid series:

$$\underbrace{C^nH^{2n+2}O}_{\text{Alcohol.}} - H^2 = \underbrace{C^nH^{2n}O}_{\text{Aldehyde.}}, \text{ and } \underbrace{C^nH^{2n}O}_{\text{Aldehyde.}} + O = \underbrace{C^nH^{2n}O^2}_{\text{Acid.}}$$

Aldehydes may be regard d as derivatives: 1. Of a molecule of hydrogen HH, half the hydrogen being replaced by an oxygen-radicle: *e.g.* benzoic aldehyde or bitter-almond oil, $C^7H^6O = C^7H^5O.H.$—2. Of a molecule of water, half the hydrogen being replaced by a monatomic hydrocarbon, *e. g.* benzoic aldehyde = $\left.\begin{matrix}C^7H^5\\H\end{matrix}\right\}O$; acetic aldehyde = $\left.\begin{matrix}C^2H^3\\H\end{matrix}\right\}O$.—3. Of a molecule of water, in which the whole of the hydrogen is replaced by a diatomic hydrocarbon: *e. g.* acetic aldehyde = $(C^2H^4.)''O$. According to this last view, which is strongly corroborated by the action of sulphuric acid and chloride of zinc upon glycol (p. 102), the aldehydes are isomeric with the ethers or anhydrides of the diatomic alcohols, and are related to them in the same manner as the dibasic anhydrides to the dibasic acids; thus

Type	H^4O^2	Type	H^2O
Sulphuric acid	$\left.\begin{matrix}SO^2\\H^2\end{matrix}\right\}O^2$	Sulphuric anhydride	$SO^2.O$
Glycol	$\left.\begin{matrix}C^2H^4\\H^2\end{matrix}\right\}O^2$	Aldehyde	$C^2H^4.O.$

The following are the aldehydes at present known.

1. Aldehydes of the form $C^nH^{2n}O = \left.\begin{matrix}C^nH^{2n-1}\\H\end{matrix}\right\}O = C^{2n}H^{2n-1}O.H.$

Acetic aldehyde	C^2H^4O	Caprylic aldehyde [?]	$C^8H^{16}O$
Propionic ,,	C^3H^6O	Enodic ,,	$C^{11}H^{22}O$
Butyric ,,	C^4H^8O	Lauric ,,	$C^{12}H^{24}O$
Valeric ,,	$C^5H^{10}O$	Palmitic ,,	$C^{16}H^{32}O$
Œnanthylic ,,	$C^7H^{14}O$		

2. Aldehyde of the form $C^nH^{2n-2}O = \left.\begin{matrix}C^nH^{2n-3}\\H\end{matrix}\right\}O = C^nH^{2n-3}O.H.$

Acrylic aldehyde, or Acrolein, C^3H^4O.

3. Aldehyde of the form $C^nH^{2n-4}O = \left.\begin{matrix}C^nH^{2n-5}\\H\end{matrix}\right\}O = C^nH^{2n-5}O.H$

Campholic aldehyde, or Camphor, $C^{10}H^{16}O$.

4. Aldehydes of the form $C^nH^{2n-8}O = \left.\begin{matrix}C^nH^{2n-9}\\H\end{matrix}\right\}O = C^nH^{2n-9}O.H.$

Benzoic aldehyde, or Bitter-almond oil, C^7H^6O.
Cuminic aldehyde, or Oil of Cumin, $C^{10}H^{12}O$.

5. Aldehyde of the form $C^nH^{2n-10}O = \left.\begin{matrix}C^nH^{2n-11}\\H\end{matrix}\right\}O$, or $C^nH^{2n-11}O.H.$

Cinnamic aldehyde, or Oil of Cinnamon, C^9H^8O.

6. Aldehydes of the form $C^nH^{2n-8}O^2 = \left.\begin{matrix}C^nH^{2n-9}O\\H\end{matrix}\right\}O$, or $C^nH^{2n-9}O^2.H.$

Salicylic aldehyde, or Salicylous acid, $C^7H^6O^2$.
Anisylic aldehyde, or Anisylous acid, $C^8H^8O^2$.

The aldehydes corresponding to known alcohols may all be formed from those alcohols by oxidation, either by exposure to the air in contact with platinum-black, or by distillation with a mixture of dilute sulphuric acid and peroxide of manganese or acid chromate of potassium. Aldehydes may also be prepared from the corresponding acids by a general process, viz. by distilling a mixture of the barium-salt of the acid with an equivalent quantity of formate of barium, thus:

$$\underbrace{\left.\begin{matrix}C^7H^5O\\ Ba\end{matrix}\right\}O}_{\text{Benzoate of barium.}} + \underbrace{\left.\begin{matrix}CHO\\ Ba\end{matrix}\right\}O}_{\text{Formate of barium.}} = \underbrace{\left.\begin{matrix}C^7H^5O\\ H\end{matrix}\right\}}_{\text{Hydride of benzoyl.}} + \underbrace{\left.\begin{matrix}CO\\ Ba^2\end{matrix}\right\}O^2}_{\text{Carbonate of barium.}}$$

(**Limpricht**, Ann. Ch. Pharm. xcvii. 368; **Piria**, Ann. Ch. Phys. [3] xlviii. 113). This process is a particular case of Williamson's method of producing compound acetones (p. 31).

Several aldehydes, as benzoic, acetic, propionic, butyric, &c. are produced by the distillation of albumin, fibrin, casein, and gelatin with peroxide of manganese and sulphuric acid. Some are formed in the destructive distillation of organic acids, as acetic aldehyde from lactic acid, œnanthylic aldehyde from ricinolic acid. Caprylic aldehyde is said by some chemists to be produced (together with the corresponding alcohol), by distilling ricinolic acid with excess of potash. According to **Bouis** (Compt. rend. xli. 603), a new acid, $C^{10}H^{18}O^2$, is formed at the same time:

$$\underbrace{C^{18}H^{34}O^3}_{\text{Ricinolic acid.}} = \underbrace{C^8H^{16}O}_{\text{Caprylic aldehyde.}} + C^{10}H^{18}O^2.$$

But according to **Malaguti** (Cimento, iv. 401), the acid formed is sebacic acid thus:

$$\underbrace{C^{18}H^{34}O^3}_{\text{Ricinolic acid.}} + 2O = \underbrace{C^8H^{16}O}_{\text{Caprylic aldehyde.}} + \underbrace{C^{10}H^{18}O^4}_{\text{Sebacic acid.}}$$

This decomposition is supposed to take place simultaneously with that by which octylic (caprylic) alcohol is produced (p. 97). The aldehyde might indeed be produced by oxidation of the alcohol. According to **Städeler**, on the other hand (J. pr. Chem. lxxxiii. 241), the product $C^8H^{16}O$ thus formed is not caprylic aldehyde, but methyl-œnanthyl, $CH^3.C^7H^{13}O$, a body isomeric with it (p. 97).

Many aldehydes are obtained directly from plants, either existing ready formed in the plants, or being given off as volatile oils on distilling the plants with water. Thus, benzoic aldehyde constitutes the essential part of bitter-almond oil, cinnamic aldehyde of cinnamon oil, cuminic aldehyde of Roman cumin oil, and salicylic aldehyde or salicylous acid, of oil of spiræa. Oil of rue consists principally of euodic aldehyde, mixed with a small quantity of lauric aldehyde (C. G. **Williams**, Proc. Roy. Soc. ix. 167). It was formerly supposed to be capric aldehyde. Benzoic aldehyde is also produced by the action of nascent hydrogen (evolved by the action of zinc on hydrochloric acid) on cyanide of benzoyl, hydrocyanic being formed at the same time:

$$C^7H^5O.Cy + HH = C^7H^5O.H + CyH.$$

This mode of formation corresponds with the representation of aldehydes as hydrides of acid radicles.

All the known aldehydes (except palmitic aldehyde, which is a fatty solid) are liquids, which volatilise without decomposition. They are very prone to oxidation, being converted into acids more or less quickly by mere exposure to the air. In consequence of this tendency to oxidation, they easily reduce the oxides of the noble metals (see p. 106). Many aldehydes are converted by hydrate of potassium, especially in alcoholic solution, into the corresponding alcohols, and the potassium-salt of the corresponding acid: thus, with bitter almond oil:

$$\underbrace{2C^7H^6O}_{\text{Benzoic aldehyde.}} + KHO = \underbrace{C^7H^8O}_{\text{Benzyl-alcohol.}} + \underbrace{C^7H^5KO^2}_{\text{Benzoate of potassium.}}$$

Cuminic aldehyde and anisylic aldehyde are decomposed in like manner. The aldehydes of the first series (corresponding to the fatty acids) and acrylic aldehyde, are not decomposed in this manner: acetic aldehyde treated with potash yields acetate and formate of potassium and a brown resinous mass.

All aldehydes form definite, and for the most part crystalline, compounds with the acid sulphites of the alkali-metals, *e. g.* bitter-almond oil with acid sulphite of sodium,

$C^7H^6O.SO^3NaH = \left.\begin{matrix}C^7H^5\\Na\end{matrix}\right\}SO^3 + H^2O = \left.\begin{matrix}SO\\Na.C^7H^5\end{matrix}\right\}O^2 + H^2O$. These compounds are for the most part soluble in water and alcohol, but insoluble in saturated solutions of the alkaline bisulphites. Hence by shaking a liquid containing an aldehyde with excess of such a saturated solution, the aldehyde may be completely separated in the form of a crystalline compound. This is an excellent method of purifying those volatile oils which have the constitution of aldehydes. The acid sulphites of potassium and sodium are, generally speaking, the best adapted for this purpose, as the compounds which they form with the aldehydes are much less soluble in the solution of the sulphite than the corresponding ammonium-compounds, and therefore crystallise more readily. From all these compounds, the aldehyde may be set free by the action of the stronger acids, or by neutralisation with an alkaline carbonate, and may then be obtained in the pure state by distillation.

The aldehydes of the first series combine with ammonia, forming crystalline compounds like aldehyde-ammonia, $C^2H^4O.NH^3$, (p. 106), and valeral-ammonia, $C^5H^{10}O.NH^3$. These compounds treated with sulphuretted hydrogen yield sulphur-bases, like thialdine, $C^6H^{13}NS^2$, and valeraldine, $C^{15}H^{31}NS^2$, thus:

$$3(C^5H^{10}O.NH^3) + 3H^2S = C^{15}H^{31}NS^2 + (NH^4)^2S + 3H^2O.$$

Heated with hydrocyanic and hydrochloric acids, they yield bases similar to the last, but containing oxygen in place of sulphur: *e. g.*:

$$C^5H^{10}O.NH^3 + CNH + ClH + H^2O = \underbrace{C^6H^{13}NO^2}_{\text{Leucine.}} + NH^4Cl.$$

Acrylic aldehyde appears also to combine directly with ammonia, forming a white amorphous compound.

The remaining aldehydes yield with ammonia peculiar amides called hydramides, the formation of which is attended with elimination of 3 atoms of water, *e. g.*

$$\underbrace{3(C^7H^6.O)}_{\substack{\text{Benzoic}\\\text{aldehyde.}}} + N^2H^6 = \underbrace{N^2(C^7H^6)^3}_{\substack{\text{Hydrobenza-}\\\text{mide.}}} + 3H^2O$$

$$\underbrace{3(C^7H^6O^2)}_{\substack{\text{Salicylic}\\\text{aldehyde.}}} + N^2H^6 = \underbrace{N^2(C^7H^6O)^3}_{\text{Salhydramide.}} + 3H^2O$$

Aldehydes also combine with anhydrous acids (anhydrides), forming compounds which are isomeric, but not identical with the diacid glycol-ethers. Thus acetic aldehyde unites with anhydrous acetic acid, forming the compound, $C^2H^4O.C^4H^6O^3$, isomeric with acetate of ethylene, $C^2H^4.(C^2H^3O)^2.O^2$;—also with anhydrous benzoic and succinic acids. Valeral forms with anhydrous acetic, and benzoic acids, the componnds $C^5H^{10}O.C^4H^6O^3$ and $C^5H^{10}O.C^{14}H^{10}O^3$, isomeric with acetate and benzoate of amylene, $C^5H^{10}.(C^2H^3O)^2.O^2$ and $C^5H^{10}.(C^7H^5O)^2.O^2$. These compounds heated with caustic alkalis yield acetates, benzoates, &c., of the alkali-metals, and reproduce the original aldehydes, whereas the acetates, benzoates of ethylene, amylene, &c., under the same circumstances, yield glycols, or hydrates of ethylene, amylene, &c. (Geuther, Ann. Ch. Pharm. cvi. 249; Guthrie u. Kolbe, ibid. cix. 296.)

The calcium and barium-salts of certain monobasic organic acids, butyric and valeric acids, for example, yield by dry distillation, together with acetones (p. 31), compounds isomeric with the aldehydes, but distinguished from them by not combining with ammonia: these compounds are called *butyral*, *valeral*, &c. (Chancel, J. Pharm. [3] vii. 143; Limpricht, Ann. Ch. Pharm. xc. 111.)

Many of the aldehydes are susceptible of polymeric transformations. Acetic aldehyde exhibits three or four such modifications (p. 108); and benzoic aldehyde is very apt to pass into the solid substance benzoin, $C^{14}H^{12}O^2$.

The acetones or ketones are aldehydes in which the basic atom of hydrogen is replaced by an alcohol-radicle, thus:

$$\text{Acetone} = \left.\begin{matrix}C^2H^3\\C\,H^3\end{matrix}\right\}O = \left.\begin{matrix}C^2H^3O\\CH^3\end{matrix}\right\}$$

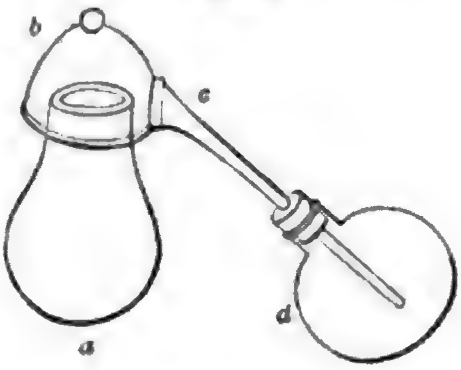
$$\text{Valerone} = \left.\begin{matrix}C^5H^9\\C^4H^9\end{matrix}\right\}O = \left.\begin{matrix}C^5H^9O\\C^4H^9\end{matrix}\right\}$$

$$\text{Valeracetone} = \left.\begin{matrix}C^5H^9\\CH^3\end{matrix}\right\}O = \left.\begin{matrix}C^5H^9O\\CH^3\end{matrix}\right\} \text{ or } \left.\begin{matrix}C^2H^3\\C^4H^9\end{matrix}\right\}O = \left.\begin{matrix}C^2H^3O\\C^4H^9\end{matrix}\right\}$$

ALDIDE. The generic name applied by L. Gmelin, in his Handbook, to the aldehydes, the latter term being by him restricted to acetic aldehyde. In Gmelin's system, the term includes several organic anhydrides and other compounds not generally regarded as aldehydes. (Handb. vii. 192.)

ALEMBIC. An apparatus for distillation, much used by the older chemists. It consists of a body *a*, to which is adapted a head *b*, of conical shape, and having its external circumference or base depressed lower than the neck, so that the vapours which rise and are condensed against the sides, run down into the circular channel formed by its depressed part, whence they pass through the nose or beak *c*, into the receiver *d*. The alembic is now scarcely used in the laboratory, being superseded by the retort, which is simpler and less expensive. Nevertheless, the alembic has its advantages. In particular the residues of distillations may be easily cleared out of the body *a*; and in experiments of sublimation, the head is very convenient to receive the dry products, while the more volatile portions pass over into the receiver. Glass alembics are now used in some manufactories of sulphuric acid for effecting the final concentration of the acid.

Fig. 4.



ALEMBROTH-SALT. A name given by the alchemists to one of the double chlorides of mercury and ammonium, $2(NH^4Cl.HgCl) + H^2O$, also called *Salt of wisdom*.

ALEXANDRITE. (See CHRYSOBERYL.)

ALGAROTH (Powder of). The alchemical name for the oxychloride of antimony, produced by throwing the chloride (butter of antimony) into water.

ALGERITE.—A hydrated silicate of alumina, occurring in New Jersey, and crystallising, sometimes in right, sometimes in oblique prisms. The following analyses of it have been given by Hunt and Crossley:

Silica	52·16	52·00
Alumina	26·08	25·42
Sesquioxide of Iron	1·94	1·54
Magnesia	1·21	5·39
Potash	10·69	10·38
Water	7·92	5·27
	100	100·00

ALIMENTARY SUBSTANCES. (See NUTRITION.)

ALISMIN. An acrid, bitter extract, probably a mixture of several compounds, obtained from the water-plaintain (*Alisma Plantago*) (Jach, Repert. Pharm. iv. 174; vi. 246.)

ALIXIA-CAMPHOR. A crystalline substance, sometimes deposited on the inner surface of the bark of *Alixia aromatica*. The crystals are white and capillary, with a slight aromatic taste and the agreeable odour of the plant. They sublime undecomposed between 70° and 80°C., but at higher temperatures they melt and form a brown substance. They are insoluble in cold, but soluble in warm water, forming a neutral solution, which deposits the crystals unaltered; so likewise does the distillate obtained from this solution. They dissolve readily in alcohol of 80 per cent., in ether, oil of turpentine, caustic potash, carbonate of potassium, and caustic ammonia. Nitric acid of sp. gr. 1·2 does not dissolve, but merely colours them yellow. (Handwört. d. Chem. i. 431.)

ALIZARIC ACID. Obtained by Schunck by the action of nitric acid on alizarin, and shown by Wolff and Strecker to be identical with Laurent's phthalic acid (which see.)

ALIZARIN. $C^{10}H^6O^3 + 2H^2O$ [or $C^{20}H^6O^6 + 4HO$]. *Lizaric acid.*—A red colouring matter obtained from madder. It was first prepared by Robiquet and Colin (Ann. Ch. Phys. [2] xxxiv. 225), who obtained it by digesting pounded madder with water at 15° or 20° C., exhausting the gelatinous extract thereby obtained with alcohol, and treating the alcoholic solution, after concentration, with dilute sulphuric acid. A precipitate was thereby obtained, which, when washed, dried, and sublimed, yielded alizarin in long, brilliant needles, having the red colour of native chromate of lead. Alizarin is identical with Runge's *madder-red* (J. pr. Chem. v. 362), and with the somewhat impure *matière colorante rouge*, obtained from madder by Persoz and Gaultier de Claubry (Ann. Ch. Phys. [2] xlviii. 69), and has been prepared in the pure state by Schunck (Ann. Ch. Pharm. lxvi. 174), by Debus (ibid. lxv. 351), and by Wolff and Strecker (ibid. lxxv. 1). It appears not to exist ready formed in madder, but to be produced by the decomposition of rubian and ruberythric acid. (See MADDER.)

Preparation according to Wolff and Strecker.—Madder is exhausted with boiling water; the decoction is precipitated by sulphuric acid; and the washed precipitate while yet moist, is boiled with a concentrated solution of alumina in hydrochloric acid, which dissolves the colouring matters, and leaves a dark brown residue. The solution mixed with hydrochloric acid deposits red flakes, consisting of alizarin, more or less contaminated with purpurin and resinous matters. This precipitate is dissolved in alcohol, or in dilute ammonia, and the solution is treated with hydrate of alumina, which unites with the colouring matters; and the alumina-compound thus formed is boiled with carbonate of soda, which dissolves the purpurin and leaves the alizarin in combination with the alumina. Lastly, this compound, after being freed from resinous matters by digestion in ether, is decomposed by hot hydrochloric acid which dissolves the alumina; and the alizarin thus separated is washed, dried by simple exposure to the air, and purified by repeated crystallisation from alcohol.

According to Schwartz (Bull. de la Soc. industr. de Mulhouse, 1856, No. 135), the purest alizarin is obtained by subliming on paper an alcoholic extract of madder having at least 35 times the colouring power of the root itself. According to Plessy and Schützenberger (Compt. rend. xliii. 167), when an extract of madder prepared with wood-spirit, is triturated with a tenfold quantity of water, and heated to 250° in a closed vessel, the water on cooling becomes filled with crystals of alizarin; and the fused extractive mass remaining at the bottom of the vessel, yields, when again treated in the same manner, an additional quantity of very pure alizarin.

Anderson, by treating opianic acid ($C^{10}H^{10}O^{5}$ = alizarin + $2H^{2}O$) with sulphuric acid, obtained a colouring matter (probably alizarin), which yielded all the madder colours with alumina and iron mordants. (Edinb. Phil. Trans. xxi. 1, 204.)

Alizarin in the anhydrous state forms red prisms, inclining more or less to yellow, according to the size of the crystals. It combines with 2 at. water, forming scaly crystals like mosaic gold. These crystals give off their water at 100 °C., becoming opaque and of a darker colour. At 215° the compound sublimes, yielding a crystalline sublimate of the same composition as alizarin dried at 100°; nevertheless a considerable quantity of charcoal is always left behind.

The following are the mean results of the analyses of alizarin dried between 100° and 120° or sublimed:

	Calculation.		Robiquet.	Schunck.	Debus.	Rochleder.
10 C . .	120	68·96	69·72	69·4	68·96	67·93
6 H . .	6	3·45	3·74	4·0	3·78	3·77
3 O . .	48	27·59	26·54	26·6	27·26	28·30
$C^{10}H^{6}O^{3}$	174	100·00	100·00	100·0	100·00	100·00

Shunck assigns to crystallised alizarin the formula $C^{14}H^{5}O^{4} + 2HO$. According to the formula $C^{10}H^{6}O^{3}$, alizarin is closely related to Laurent's chloronapthalic acid, $C^{10}H^{5}ClO^{3}$. The latter, when boiled with nitric acid, yields phthalic and oxalic acid, like alizarin (*vid. inf.*).

Alizarin dissolves but sparingly in water, even at the boiling heat; but according to Plessy and Schützenberger (*loc. cit.*) its solubility is much increased by heating to higher temperatures in close vessels, 100 pts. of water dissolve 0·034 pt. of alizarin at 100° C.; 0·035 at 150°; 0·82 at 200°; 1·70 at 225°; and 3·16 pts. at 250°.

Alcohol and ether dissolve it, forming yellow solutions. It is not decomposed by hydrochloric acid. Strong sulphuric acid dissolves it, forming a brown solution from which the alizarin is precipitated by water in orange-coloured flakes. Nitric acid at the boiling heat dissolves it, with evolution of red vapours, forming phthalic acid and probably also oxalic acid (Wolff and Strecker):

$$\underbrace{C^{10}H^{6}O^{3}}_{\text{Alizarin.}} + H^{2}O + 4O = \underbrace{C^{8}H^{6}O^{4}}_{\text{Phthalic acid.}} + \underbrace{C^{2}H^{2}O^{4}}_{\text{Oxalic acid.}}$$

It is also converted into phthalic acid by boiling with ferric chloride or nitrate (Schunck). Chlorine converts it, when suspended in water, into a yellow substance which dissolves in alkalis without much colour, and yields a colourless sublimate when heated.

Alizarin dissolves in caustic alkalis and in alkaline carbonates, forming deep purple solutions, from which it is precipitated by acids in orange-coloured flakes. The ammoniacal solution gives off all its ammonia by evaporation, and forms with the chlorides of barium and calcium purple precipitates which become nearly black when dry. The potash solution is completely decolorised by lime-water, a precipitate being formed containing $2C^{10}H^{6}O^{3}.3CaHO$, or $2C^{20}H^{6}O^{6}.3(CaO,HO)$. With baryta, in a similar manner, two compounds are formed, viz. $2C^{10}H^{6}O^{3}.3BaHO$ and $C^{10}H^{6}O^{3}.2BaHO$. Alumina decolorises an alcoholic solution of alizarin, forming a beautiful red lake. An ammoniacal solution of alizarin forms with salts of magnesium, iron, copper, and silver, purple precipitates with a red or bluish iridescence. The silver precipitate becomes reduced after some time. The alcoholic solution of alizarin forms with an alcoholic solution of acetate of lead, a purple precipitate containing $4C^{10}H^{5}PbO^{3}.3Pb^{2}O$, or $2C^{20}H^{5}PbO^{6}.3PbO$, according to Schunck, and $3C^{10}H^{6}O^{3}.2Pb^{2}O$, according to Debus.

ALIZITE. (See PIMELITE.)

ALKALI. *Alcali*, *Laugensalz*. The word *alkali* is used in various senses. In its most restricted, but most usual sense, it is applied to four substances only: hydrate of potassium (potash), hydrate of sodium (soda), hydrate of lithium (lithia), and hydrate of ammonium (which may be supposed to exist in the aqueous solution of ammonia). In a more general sense, it is applied to the hydrates of the so-called *alkaline earths* (baryta, strontia, and lime), and to a large number of organic substances both natural and artificial, which are more fully described in the articles ALKALOIDS and AMMONIUM-BASES. The first four bodies are sometimes spoken of as *alkalis proper*, when it is wished specially to distinguish them from the other alkalis.

As the individual alkalis are described with sufficient detail in the articles specially devoted to each, we shall confine this article to a discussion of those properties which they all possess in common; in order, as far as possible, to define the essential nature of alkalinity, and to point out upon what grounds this or that particular body is classed as an alkali. These objects will probably be best attained by tracing the most important of the successive steps by which the word alkali, which was at first the name of a single substance, has come to be the generic name of an indefinite number of bodies.

The term alkali was first used in chemistry to designate the soluble part of the ashes of plants, especially of sea-weed (carbonates of sodium and potassium). It was, however, soon extended to several similar substances which were obtained by other processes: for instance, to salt of tartar, and to carbonate of potassium obtained by heating nitre with charcoal. The substances obtained by these processes, and by others of like nature, were regarded as identical, or at most, as mere varieties of the same substance. Alkali was, therefore, not yet used as a generic name, but as the specific name of a particular substance. The character which was chiefly depended upon for distinguishing alkali from other substances was the property of effervescing with acids. This property was supposed to be characteristic of, and essential to, alkaline bodies, till after the middle of the 18th century. Another property of alkali which was early observed was its opposition to acids, and power of destroying their most distinctive characters. On account of its possessing these properties, carbonate of ammonium, which had been known since the thirteenth century, was, from the beginning of the seventeenth century, regarded as a kind of alkali. The power of alkali to change many vegetable colours was recognised at a later period than the properties above mentioned, but was well known to Boyle, who also knew that colours which had been thus altered could be restored by acids.

It was first clearly established in 1736, by Duhamel, that there existed two essentially distinct kinds of fixed alkali. From this time, three kinds of alkali were recognised, — vegetable alkali, mineral alkali, and volatile alkali, corresponding respectively to potash, soda, and ammonia, or to their carbonates.

We have already said that, far on in the eighteenth century, the power of effervescing with acids was regarded as an essential property of alkalis. Boyle had indeed observed, in 1684, that volatile alkali could be obtained by distillation over quick lime in a condition in which it no longer effervesced with acids, although it retained all its other usual properties. But, notwithstanding isolated observations of this kind, non-effervescing alkalis were regarded rather as subordinate varieties of the ordinary alkalis than as essentially different substances.

Moreover, it was known at a very early date, that quick lime altered some of the properties of alkali. This alteration was expressed by calling alkali, which had not been acted on by lime, *mild*, and alkali which had been so acted on, *caustic*. The effect of the lime was ascribed by Basil Valentine (latter half of the fifteenth century) to heat ("die Hitze aus dem lebendigen Kalk") which it imparted to the alkali. And the idea that lime in burning combined with an active principle — "matter of fire" — which it gave out again partially to water (when slaked), and completely to alkali, remained long dominant. Van Helmont (circ. 1640) regarded the substance taken up by lime as a kind of sulphuric acid, whence the heat evolved in the action of water on quick lime. Meyer, as recently as 1764, supposed the lime-salt of a peculiar acid, *acidum pingue*, to be formed during the burning of lime, and that when this salt was treated with a mild alkali, a corresponding alkaline salt (caustic alkali) was obtained. The greasy feel of the caustic alkalis suggested the name of the acid which Meyer supposed them to contain.[*]

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[*] It is a remarkable illustration of the change which takes place in the ideas attached to the same word, that both Van Helmont and Meyer should have attributed what we consider an exaltation of the *alkaline* property to the agency of an *acid*. (See ACIDS, p. 40.)

The true nature of the difference between caustic and mild alkalis was discovered by Black in 1755. Black's investigation of this subject occupies so important a place in the history of general chemical theory, that it is worth while to consider a little in detail his experiments and the conclusions he derived from them.

His first observation was that quick lime, when deadened by exposure to air, became heavier, not lighter, as was to be expected, if the change which took place consisted in the escape of *fire-matter*. He made a similar observation in the case of magnesia (a substance which he had previously found to be distinct from lime). He found further that magnesia, in the state in which it effervesces with acids, lost considerably in weight when calcined, and that it then no longer effervesced with acids, although it formed with them salts exactly similar to those of effervescing magnesia. In order to find out what was the substance which effervescing magnesia lost when calcined, he repeated the calcination in a retort connected with a well cooled receiver. In this experiment, he obtained nothing but a small quantity of water; it occurred to him, however, that a gas might have escaped, and that this gas might be the same as that which is evolved during the solution of *magnesia alba* (effervescing magnesia) in acids. Following out this supposition, he came to the conclusion that the effervescing magnesia which is precipitated by a mild alkali from a solution of calcined (not effervescing) magnesia in acid, could obtain the gas, which caused it to effervesce when dissolved, from no source except the alkali. Hence he concluded further that the mild alkalis contain the same gas as is expelled from *magnesia alba* by calcination; that, when they combine with acids, this gas is separated and causes effervescence; and that, when a magnesia salt is precipitated by a mild alkali, the gas leaves the latter and unites with the magnesia, in combination with which it is precipitated. These conclusions were verified by the following quantitative experiment. A weighed quantity of *magnesia alba* was calcined; it then dissolved in sulphuric acid without effervescence. The solution was precipitated by mild vegetable alkali (carbonate of potassium), the precipitate washed, dried, and weighed: its weight was almost exactly the same as that of the original *magnesia alba*, and it behaved in every respect like that substance. On a further examination of the gas, which is expelled by acids from the mild alkalis and lime, and from *magnesia alba*, Black found it to be the same as that which is formed during fermentation, and gave it the name *fixed air*.

From the sum of his observations, Black deduced the following general conclusions. The effervescing earths and alkalis contain fixed air, which can be expelled from the former by heat, though not from the latter, but which is expelled from both by acids; the alkalis and earths are caustic when they contain no fixed air, and therefore their causticity does not depend on the presence of any peculiar constituent, but is a property possessed by them in a state of purity; quick lime renders the alkalis caustic, not by imparting to them any principle of causticity, but by the removal from them of fixed air; lastly fixed air partially neutralises the alkalis by combining with them, insomuch as it destroys their causticity.

Two of the most important effects which the adoption of Black's theory had upon the received ideas of alkalinity were that it caused chemists to perceive (which they had not done before), a necessary opposition between the causticity of an alkali and its power of effervescing with acids, and caused the term alkali to be transferred from the carbonated to the caustic alkalis.

Besides the substances to which the name alkali was first given, it was soon perceived that certain kinds of earth possessed, in some degree, alkaline properties; that is to say, the power of effervescing when acted on by acids, and of neutralising their acid properties. Earths which possessed these qualities were called *terræ absorbentes*, or *terræ alcalinæ*, and were long supposed to owe their peculiarities to the presence of alkali as one of their constituents.

It is not easy to make any precise statement as to the degree of similarity or of difference which was supposed to exist between these bodies and alkali proper. The difficulty arises partly from the fact, that, until they had acquired some idea of the principles of chemical analysis, chemists had no sure means of ascertaining the identity or individuality of chemical substances, and hence often called different bodies by the same name, or, on the other hand, gave different names to the same substance when obtained by different processes; partly also, from the word alkali having been used formerly as now in various senses: by Lemery, for instance, to include all substances which effervesce with acids; by Stahl, to include all those which neutralise acids; by many others, however, to denote none but the substances now known as the alkaline carbonates. This uncertainty in the use of the word is not surprising, when we remember that our present more extensive knowledge does not enable us to point out any one difference of fundamental importance between the alkalis and the alkaline earths. The different solubility in water of their carbonates probably furnishes a more exact distinction than any other single property. This character was pointed out by

Duhamel in 1736, as a generic difference. He distinguished earths from alkalis by the property which the latter have of precipitating the former from their solutions, and the alkaline earths from others by their capability of completely neutralising acids. These distinctions have, for the most part, been ever since retained.

It is not necessary to discuss with much detail early ideas relating to the ultimate constitution of the alkalis and alkaline earths. A similarity of constitution between the earths and metallic calces was soon suspected; in consequence of which Neumann, before the middle of the eighteenth century, endeavoured to get a metal from quick lime. By the later phlogistic chemists, both alkalis and earths were, like metallic calces, regarded as simple bodies. Lavoisier, though he regarded metallic calces as compounds, continued to class the alkalis and earths among elementary bodies, inasmuch as there was no known means of decomposing them. He considered it probable, however, that they contained oxygen, and suggested that the earths might be oxides of metals which had a greater affinity for oxygen than carbon, and therefore could not be reduced. Many attempts were made by Lavoisier's followers to verify these suppositions; but their uniform failure seemed almost to have proved the elementary nature of the bodies in question, when, in 1807, Sir Humphry Davy succeeded in reducing potash and soda by the galvanic current. The composition of volatile alkali (ammonia), was approximately ascertained by Berthollet in 1785. After the discovery of oxygen in the fixed alkalis, it was long supposed by Davy and Berzelius that ammonia also contained oxygen. The idea that aqueous ammonia contained the oxide of a compound metal, which likewise existed in the ammonia-salts, was suggested by Berzelius in 1820. (See AMMONIUM.)

In the present state of chemical theory, the relations of the alkalis to other substances lead to the representation of them as hydrates, or as water in which half the hydrogen is replaced by a metal, or compound radicle. (See TYPES.)

The earliest addition made by modern chemistry to the old list of alkalis was morphia, discovered in opium by Sertürner in 1805, but first fully described by him in 1817. This was the first organic alkali, or alkaloid which became known; but, when the general attention of chemists was directed to its existence, it was soon found to be one of a very numerous class of compounds (see ALKALOIDS). Of late years, a large number of bodies, possessing many points of resemblance to the natural alkaloids have been obtained by artificial processes. The constitution of these artificial alkalis is similar to that of hydrate of ammonium: they represent hydrate of ammonium in which hydrogen is replaced by an electro-positive radicle (in most cases a hydrocarbon), (see AMMONIUM-BASES), or in which nitrogen is replaced by phosphorus, arsenic, or antimony.

The following properties are common to the mineral alkalis and to many of the organic alkalis.

(1) They are more or less soluble in water, the alkalis proper much more so than the alkaline earths. (2) They neutralise completely the strongest acids, and with weak acids form salts possessing in some degree, alkaline properties. (3) Their aqueous solutions exert a caustic or corrosive action on vegetable and animal substances; (4) precipitate the heavy metals from most of their acid solutions as hydrates or as oxides; (5) and alter the tint of many colouring matters; for instance, they turn litmus, which has been reddened by acid, blue, they turn turmeric brown, and syrup of violets and infusion of red cabbage, green. The extent to which the various alkalis dissolve in water appears to determine the degree in which they possess the last three properties (3, 4, 5), the most soluble possessing them in a greater degree than the rest. The action on colouring matters appears to belong to all metallic hydrates which are soluble in water, and is possessed by the hydrates of lead, silver, and mercury, in a degree corresponding to their slight solubility.

(For further historical details concerning alkalis and alkaline earths, see Kopp, Geschichte der Chemie, vols. iii. and iv.). — G. C. F.

ALKALIMETRY is the determination of the amount of real alkali in alkaline mixtures and liquids, such as the commercial carbonates of potassium and sodium, (commonly called potash and soda), in wood-ashes, solutions of caustic and carbonated alkalis, &c. This estimation, like that of the strength of acids, may be made either by volumetric or by weight-analysis.

The volumetric method of alkalimetry is merely a particular case of the general method of "Analysis by Saturation," described in the article ANALYSIS, VOLUMETRIC (which see). The valuation of an alkali by the amount of a standard acid solution which it will saturate, was first introduced by Descroizille, afterwards perfected by Gay-Lussac, and still further by Mohr. (Lehrbuch der chemisch-analytischen Titrirmethode, Braunschweig, 1855.)

Instead of the sulphuric or hydrochloric acid generally used for the purpose, Mohr recommends oxalic acid, because it can be weighed with greater accuracy than any liquid acid, and because its standard solution may be kept for any length of time without change. To obtain it pure, the commercial acid, which is generally contaminated with the oxalates of potassium and calcium, is finely pounded, and treated with a quantity of lukewarm water sufficient to dissolve only a portion of it; the solution is filtered and left to crystallise; and the crystals are collected on a filter and dried in the air, till they no longer adhere to each other or to the paper. The acid is thus obtained pure, and containing exactly $C^2H^2O^4 + 2H^2O$, the atomic weight of which is 126.

The standard solution is best made of such a strength that 1000 cubic centimetres (1 litre), shall contain exactly one $\frac{1}{2}$-gramme-atom (*i.e.* 1 atom expressed in $\frac{1}{2}$-grammes) of the acid. This is effected by dissolving in water $\frac{126}{2} = 63$ grammes of the crystals, and diluting the solution to the bulk of 1 litre. 1000 c. c. of this solution contain one $\frac{1}{2}$-gramme-atom of acid: hence 2 c. c. contain 1 milligramme-atom of acid, and saturate 2 milligramme-atoms of a caustic alkali (KHO or NaHO), 1 milligramme of an anhydrous alkali (K^2O or Na^2O), or of an alkaline carbonate (CO^3K^2 or CO^3Na^2.)

To estimate the value of a sample of commercial potash or soda, 3 or 4 grammes of it are first ignited in a platinum crucible in order to determine the amount of water contained in it. The residue is then dissolved in water; a few drops of litmus are added; and the standard acid is gradually added from a burette till the first appearance of a purple-red or wine-red colour. This takes place when a little more than half the alkaline carbonate is decomposed by the oxalic acid: for the first portions of carbonic acid disengaged by the oxalic acid, unite with the remaining portion of alkaline carbonate to form acid carbonate, and it is only when half the alkali has been neutralised in this way that the carbonic acid is actually set free and reddens the litmus. After this stage has been attained, the oxalic acid must be very cautiously added till the purple-red produced by the carbonic acid, just passes into a bright yellowish-red, indicating the presence of free oxalic acid, and showing that the whole of the alkali is neutralised by that acid. Each c. c. of acid thus employed corresponds to 1 milligramme of caustic alkali, or to one $\frac{1}{2}$-milligramme of alkaline carbonate, *i.e.* to 0·040 grm. caustic soda (NaHO), 0·056 grm. caustic potash (KHO), 0·069 grm. carbonate of potassium (CO^3K^2), and 0·053 grm. of carbonate of sodium. The amount of caustic alkali or alkaline carbonate is then found by a simple proportion; thus:

100 : 5·3 : : number of c. c. employed : amount of carbonate of sodium.

By operating on 100 times the $\frac{1}{2}$-milligramme-atom (*e.g.* 6·9 grms. of carbonate of potassium, or 5·3 grms. of carbonate of sodium), all calculation is saved: for as this amount, if perfectly pure, would require 100 c. c. of acid for its saturation, the number of c. c. actually required indicates at once the percentage of alkaline carbonate. The burettes commonly used contain 50 c. c., and are graduated into half c. c.; so that by operating on 50 times the $\frac{1}{2}$-milligramme-atom, the number of divisions employed indicates the percentage.

In operating upon alkaline carbonates in the manner just described, it is difficult to notice the exact moment when the wine-red colour of the litmus due to the presence of free carbonic acid, changes to the light red produced by oxalic or other strong acid. For this reason Mohr recommends the following, called the *residual method*. The standard acid is added till the colour of the litmus is distinctly bright red; the solution is then heated to boiling, and a slight excess (5 to 10 c. c.) of acid is added. The hot solution is freed from carbonic acid by agitation and by drawing air through it by means of a glass tube, and then neutralised with a standard solution of caustic soda (ANALYSIS, VOLUMETRIC), till the colour just changes from red to blue. Since the acid and alkaline solutions neutralise each other, volume for volume, it is only necessary to deduct the number of cubic centimetres employed of the latter from that of the former, and calculate the amount of alkali from the residue. In estimating the strength of caustic alkaline solutions, this residual method is of course unnecessary.

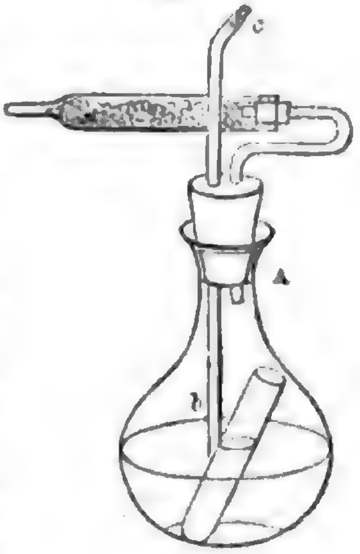
To determine the proportion of caustic alkali and alkaline carbonate in a mixture of the two, two equal portions of the solution must be taken: one of them treated with chloride of barium, whereby the alkaline carbonate is converted into chloride, and carbonate of barium is precipitated. The liquid is filtered and the quantity of caustic alkali determined in the filtrate as above. The second portion of the solution is neutralised with the standard acid, without previous treatment with chloride of barium, and the total amount of alkali, existing both in the caustic state and as carbonate, is thereby determined. The first result deducted from the second, gives the quantity of alkali existing as carbonate.

If it be preferred to make these estimations with the ordinary English weights and measures, the standard solution of oxalic acid may be made by dissolving 63 grains ($\frac{1}{2}$-grain-atom) of the crystallised acid in water and diluting the solution to 1000 grain-measures at 60° F. This quantity of the solution will then neutralise 1 grain-atom of a caustic alkali (40 grains of soda NaHO, or 56 grains of potash KHO), and $\frac{1}{2}$-grain-atom of alkaline carbonate (69 grains of CO^3K^2, or 53 grains of CO^3Na^2), and by operating on $\frac{1}{10}$ of these quantities of the substance to be tested, the percentages will be given at once by the number of grain-measures of the standard acid employed.

A convenient method of estimating by volumetric analysis the proportion of potash and soda in a caustic mixture of the two, has been kindly communicated to the Editor by Mr. John Dale of Cornbrook, near Manchester. It depends upon the fact that acid tartrate of potassium, though moderately soluble in water, is but very sparingly, if at all, soluble in a liquid containing acid tartrate of sodium. The method is as follows: Add to the mixture a standard solution of tartaric acid till an acid reaction just becomes perceptible; the alkalis are thereby converted into neutral tartrates; then add a second quantity of tartaric acid equal to the first, so as to convert them into acid tartrates: the whole (or nearly the whole) of the acid tartrate of potassium then separates. Next filter off the solution of acid tartrate of sodium, and add a standard solution of caustic soda till the liquid just exhibits an alkaline reaction. The quantity of the soda solution thus added is equal to the amount of soda present in the mixture.—The quantity of tartaric acid required to form acid tartrate with the soda, subtracted from the total quantity added to the mixture of the two alkalis, gives the quantity required to form acid tartrate with the potash; and thus the amount of potash is determined. This method would scarcely be applicable where scientific accuracy is required; but, for rapid estimation in commercial practice, it is found to give good results.

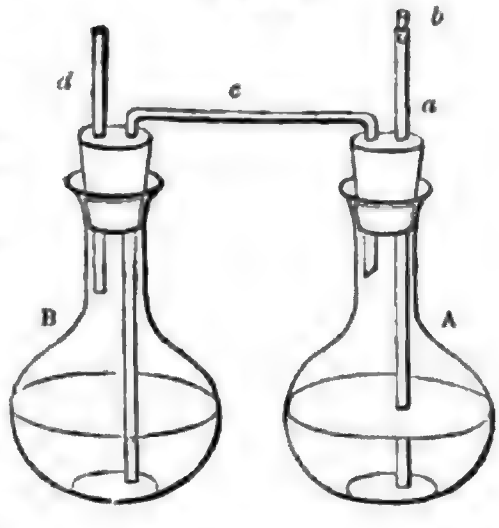
Alkalimetry by Weight-analysis.—The proportion of alkali in the commercial carbonates of potassium and sodium may be estimated by determining the quantity of carbonic anhydride evolved when the carbonates are decomposed by an acid: for 22 parts of carbonic anhydride (CO^2) correspond to 69 parts of carbonate of potassium (CO^3K^2), and to 53 parts of carbonate of sodium (CO^3Na^2). The apparatus employed is the same as that described in the article ACIDIMETRY; but the method of using it is slightly different. A weighed quantity of the carbonate to be examined is dissolved in warm water in the flask A, and a quantity of hydrochloric or dilute sulphuric acid more than sufficient to decompose the carbonate, is placed in a short test-tube *b*, which is carefully introduced into the flask, so that it may rest against the side. The apparatus having been then weighed, the extremity of the tube *c* is closed by a plug of wax, and the flask is tilted so that the acid may run over into the alkaline liquid. When the evolution of gas ceases, the flask is heated to complete the decomposition; the wax plug is removed and air drawn through the apparatus to remove the carbonic acid remaining in it; and the flask after cooling is again weighed to ascertain the loss of carbonic acid. At the conclusion of the experiment, a piece of blue litmus-paper must be thrown into the flask, to try whether the liquid is acid; if not, more acid must be added, and the process repeated.

Fig. 5.



The apparatus of Will and Fresenius (*fig.* 6) may also be used. The alkali dissolved in water is then placed in the flask A, and strong sulphuric acid in B; and the whole apparatus is weighed; the tube *a b* is closed with a wax plug; and suction is applied by the mouth at the end of the tube *d*, so as to draw a few bubbles of air from A into B. On discontinuing the suction the pressure of the air forces a small quantity of the acid in B into the flask A, whereby a portion of the alkaline carbonate is decomposed. This process is repeated as long as any gas continues to be evolved, after which the flask A is heated, and the experiment completed in the manner just decribed.

Fig. 6.



If the alkaline carbonate contains any caustic alkali, which may be known (in the absence of sulphide), by its solution having an alkaline reaction after the addition of excess of chloride of barium, another equal portion must be mixed with about one-third of its weight of carbonate of ammonium, and 3 parts of quartz-sand (to prevent caking), and heated till the water and ammonia are expelled; the dry residue is then decomposed as above. The excess of alkaline carbonate obtained in the second determination is due to the caustic alkali in the sample, which is converted into carbonate by ignition with the carbonate of ammonium; and from it the amount of caustic alkali is easily calculated; thus for soda:

$$CO^3Na^2 : 2NaHO \ [\text{or } CO^2.NaO : NaO.HO] = 106 : 80.$$

The sulphites, hyposulphites, and sulphides of the alkali-metals, which often occur in commercial samples of alkali, especially in "ball-soda," introduce errors both into the volumetric and the weight-analyses: into the former, by neutralising a portion of the test-acid, and into the latter by evolving sulphurous acid or sulphuretted hydrogen, which would be estimated as carbonic acid. When the amount of alkali is to be determined by the volumetric method, these compounds may be decomposed by igniting the substance with chlorate of potassium, whereby they are all converted into sulphates. For the carbonic acid estimation, they may be oxidised by adding a small quantity of neutral chromate of potassium to the solution in the flask, before commencing the decomposition.

The carbonates of the earths, which would introduce similar errors, may be removed by dissolving the alkaline carbonate in water and filtering.

ALKALOIDS. *Organic Alkalis, Organic Bases.*—At the beginning of this century, the only substances in which alkaline properties had been recognised were potash, soda, ammonia, and the alkaline earths (see ALKALI). In 1817, Sertürner drew attention to the existence in opium of a substance whose alcoholic solution acted upon vegetable colours like the solutions of the alkalis, which combined directly with acids, forming neutral salts, soluble in water, and giving the usual reactions of the acids from which they were formed; and which was precipitated from solutions of its salts by the mineral alkalis. To this substance, Sertürner gave the name *morphine*, and in consequence of its possessing the properties just mentioned, regarded it as a kind of alkali. After the discovery of morphine, it was soon found that many vegetable products which had been long known as exerting marked physiological effects (*e. g.* cinchona bark, nux vomica, tobacco, &c.), contained similar alkaline principles. The number of such natural *alkaloids* now known is very great, and includes many substances which cannot in any strict sense be termed alkalis, but which are connected by such insensible gradations (between intermediate terms) with substances decidedly alkaline, that they must be regarded as possessing essentially the same chemical nature as the latter. Since 1848, a great number of organic alkalis have been obtained artificially. Some of these rival potash and soda in the degree of their alkalinity, while in others the existence of alkaline properties is barely perceptible.

The only property which is possessed by all alkaloids, whether natural or artificial, is that of combining directly with acids to form salts possessing a certain degree of stability, and capable, when dissolved in water, of producing the ordinary phenomena of saline double decomposition. Those alkaloids, whose salts possess any considerable degree of stability, generally exhibit, when dissolved in water or alcohol, an alkaline reaction with vegetable colours.

Most of the natural alkaloids contain carbon, hydrogen, nitrogen, and oxygen, and are, at ordinary temperatures, solid, and not volatile without decomposition. Some natural alkaloids contain carbon, hydrogen, and nitrogen only; these are, for the most part, liquid at ordinary temperatures, and can be distilled without decomposition. The greater number of the artificial alkalis are composed of carbon, hydrogen, and nitrogen; some, however, contain oxygen in addition. In both natural and artificial alkaloids, hydrogen may be replaced by chlorine, bromine, iodine, peroxide of nitrogen, &c. Alkaloids have also been obtained artificially, in which nitrogen is replaced by phosphorus, arsenic, antimony, or bismuth. (See PHOSPHINES, ARSINES, &c.)

Most of the alkaloids, as they are obtained in the free state, correspond in composition to ammonia, NH^3, rather than to the fixed alkalis; that is to say, they form salts by direct union with acids, without elimination of water or any other substance. In order to make them strictly comparable to the fixed alkalis, they require, like ammonia, the addition of H^2O to their formulæ: they may then be considered as hydrates of compound radicles analogous to ammonium. A few alkaloids, however, are known which, when dehydrated as far as possible, correspond precisely to the fixed alkalis; *e.g.* hydrate of tetrethylium, $C^8H^{21}NO = C^8H^{20}N.H.O$. These bodies, for the most part, resemble potash and soda very closely in properties.

The constitution of most of the artificial alkaloids is tolerably well known. The processes by which they are obtained show that they must be considered as ammonia, or as hydrate of ammonium, in which the hydrogen is replaced wholly, or in part, by a compound radicle generally composed of carbon and hydrogen (see AMIDES, AMMONIUM-BASES). The phosphorus, arsenic, &c. alkaloids are similarly related to phosphide, arsenide, &c. of hydrogen, PH^3,AsH^3, &c. The constitution of the natural alkaloids is, as yet, very imperfectly understood. They are probably, like the artificial alkalis, derivatives of ammonia; but it is unknown by what radicles the hydrogen is replaced.

The following is a list of the most important nitrogen-alkaloids, natural and artificial, which are now known.

1. Alkaloids comparable to ammonia, forming salts by direct union with acids.

Name.	Formula.	Source or Mode of Formation.
Acediamine	$C^2H^6N^2$	Acetamide heated in hydrochloric acid gas.
? Acetonine	$C^9H^{18}N^2$	Action of ammonia on acetone.
Acetylamine. (See VINYLAMINE.)		
Aconitine	$C^{30}H^{47}NO^7$	*Aconitum Napellus.*
Alanine	$C^3H^7NO^2$	Hydrochloric and hydrocyanic acids on aldehydammonia.
Alkaloid	$C^3H^5N.$	Nitrous ether on creatine (Dessaignes).
Alkaloid	$C^4H^8N^4$	Distillation of ethylcyanamide (Cahours and Cloez).
Alkaloid	$C^8H^{13}NO$	From aldehydammonia (Babo).
Alkaloid	$C^{10}H^{15}NO$	
Allylamine	$C^3H^7N.$	
Dibromdiallylamine	$C^6H^9Br^2N$	Tribromide of allyl on ammonia
Ethyldibromdiallylamine	$C^8H^{13}Br^2N.$	
Amarine	$C^{21}H^{18}N^2$	Potash on hydrobenzamide.
Diethylamarine	$C^{25}H^{26}N^2.$	
Ammeline	$C^3H^5N^5O$	Strong acids or alkalis on cyanamide.
Amylamine	$C^5H^{13}N.$	
Diamylamine	$C^{10}H^{23}N.$	
Diethylamylamine	$C^9H^{21}N.$	
Methylethylamylamine	$C^8H^{19}N.$	
Triamylamine	$C^{15}H^{33}N.$	
Aniline. (See PHENYLAMINE.)		
Anisine	$C^{24}H^{24}N^2O^3$	Action of heat on anishydramide.
Aricine	$C^{23}H^{26}N^2O^4$	Cinchona bark.
Asparagine	$C^4H^8N^2O^3$	*Asparagus officinalis*, and other plants.
Atropine	$C^{17}H^{23}NO^3$	*Atropa belladonna, Datura Stramonium.*
Azonaphtylamine	$C^{10}H^{10}N^2$	Reduction of dinitronaphtalene.
Azophenylamine	$C^6H^8N^2$	Reduction of dinitrobenzine.
Bebirine	$C^{19}H^{21}NO^3$	"*Bebeeru*," a species of *Nectandra*, British Guiana.
Benzidine	$C^{12}H^{12}N^2$	Reducing agents on azobenzide and on azoxibenzide.
Berberine	$C^{21}H^{19}NO^5$	*Berberis vulgaris.*
Brucine	$C^{23}H^{26}N^2O^4$	*Strychnos nux vomica, S. Ignatii, S. Colubrina.*
Ethylbrucine	$C^{25}H^{30}N^2O^4.$	
Caffeine	$C^8H^{10}N^4O^2$	Tea, coffee, &c.
Caproylamine. (See HEXYLAMINE.)		
Caprylamine. (See OCTYLAMINE.)		
Carbamide. (See UREA.)		
Carbotriphenyltriamine, or Cyantriphenyldiamine	$C^{19}H^{17}ON^3$	Dichloride of carbon on phenylamine.
Carbothialdine	$C^5H^{10}N^2S^2$	Sulphocarbonic anhydride on aldehyd-ammonia.
Cetylamine.		
Tricetylamine	$C^{48}H^{99}N.$	
? Chelidonine	$C^{20}H^{19}N^3O^3$	*Chelidonium majus.*
Cinchonicine	$C^{20}H^{24}N^2O$	Isomeric transformation of cinchonine or of cinchonidine.
Cinchonidine	$C^{20}H^{24}N^2O$	Cinchona bark.
Methylcinchonidine	$C^{21}H^{26}N^2O.$	
Cinchonine	$C^{20}H^{24}N^2O$	Cinchona bark.
Methylcinchonine	$C^{21}H^{26}N^2O.$	
Codeine	$C^{18}H^{21}NO^3$	Opium.
Ethylcodeine	$C^{20}H^{25}NO^3.$	

Name.	Formula.	Source or Mode of Formation.
Colchiceine	$C^{34}H^{44}N^2O^{11}$	*Colchicum autumnale.*
Collidine	$C^8H^{11}N$	Bone-oil.
Conhydrine	$C^8H^{17}NO$	Hemlock (*Conium maculatum*).
Conine	$C^8H^{15}N$	Hemlock (*Conium maculatum*).
Ethylconine	$C^{10}H^{19}N$.	
Methylconine	$C^9H^{17}N$.	
Cotarnine	$C^{12}H^{13}NO^3$ *	Oxidation of narcotine.
Coumaramine	$C^9H^7NO^2$	Reduction of nitro-coumarine.
Creatine	$C^4H^9N^3O^2$	Juice of flesh.
Creatinine	$C^4H^7N^3O$	Action of acids on creatine.
Cryptidine	$C^{11}H^{11}N$	Coal-tar.
Cumidine	$C^9H^{13}N$	Reduction of nitro-cumine.
Cyanamide	CH^2N^2	Gaseous chlor. of cyanogen on ammonia.
Amylcyanamide	$C^6H^{12}N^2$.	
Diamylcyanamide	$C^{11}H^{22}N^2$.	
Diethylcyanamide	$C^5H^{10}N^2$.	
Ethylcyanamide	$C^3H^6N^2$.	
Methylcyanamide	$C^2H^4N^2$.	
Methylethylcyanamide	$C^4H^8N^2$.	
Cyanethine	$C^9H^{15}N^3$	Potassium on cyanide of ethyl.
Cyanetholine	C^3H^5NO	Chloride of cyanogen on ethylate of sodium.
Cyaniline	$C^{14}H^{14}N^4$	Do. on phenylamine (aniline.)
Cyanocumidine	$C^{20}H^{26}N^4$	Do. on cumidine.
Cyanomelamine	$C^{15}H^{13}N^5$	Do. on melaniline.
Cyanotoludine	$C^{16}H^{18}N^4$	Do. on toluidine.
Diphenine	$C^{12}H^{12}N^4$	Reduction of dinitrazobenzide.
Diphenylformyldiamine	$C^{13}H^{12}N^2$	Chloroform on phenylamine.
Ethylamine	C^2H^7N.	
Diethylamine	$C^4H^{11}N$.	
Triethylamine	$C^6H^{15}N$.	
Ethylenamine	$C^2H^8N^2$	Bromide of ethylene on ammonia.
Diethylenamine	$C^4H^{10}N^2$	
Phenylethylenamine	C^8H^9N.	Bromide of ethylene on phenylamine.
(or Diphenylbiethylenamine	$C^{16}H^{18}N^2$?	
Triethylenamine	$C^6H^{12}N^2$	Bromide of ethylene on ammonia.
Flavine	$C^{13}H^{12}N^2O$	Reduction of binitrobenzophenone.
Furfurine	$C^{15}H^{12}N^2O^3$	Furfuramide boiled with potash.
Glycocoll	$C^2H^5NO^2$	Ammonia on chlor- or bromacetic-acid.
Glycosine	$C^6H^6N^4$	Ammonia on glyoxal.
Glyoxaline	$C^3H^4N^2$	
Guanine	$C^5H^5N^5O$	Guano, &c.
Harmaline	$C^{13}H^{14}N^2O$	Seeds of *Peganum Harmala.*
Hydrocyanharmaline	$C^{14}H^{13}N^3O$	Hydrocyanic acid and harmaline.
Harmine	$C^{13}H^{12}N^2O$	Seeds of *Peganum Harmala*; also oxidation of harmaline.
Hexylamine.		
Trihexylamine	$C^{18}H^{39}N$	Sulphite of œnanthylsodium distilled with lime.
? Jervine	$C^{30}H^{46}N^2O^3$	*Veratrum album*, white hellebore.
Lepidine	$C^{10}H^9N$	Coal-tar; also quinine and cinchonine distilled with potash.
Leucine	$C^6H^{13}NO^2$	Hydrochloric and hydrocyanic acids in valeral ammonia.
Lophine	$C^{21}H^{16}N^2$	Distillation of hydrobenzamide.
Lutidine	C^7H^9N.	Bone-oil.
Melamine	$C^3H^6N^6$	Action of heat on cyanamide.

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* According to unpublished analyses by Matthiessen and Foster.

Name.	Formula.	Source or Mode of Formation.
Melaniline	$C^{13}H^{13}N^{3}$	Cyananilide (cyanophenylamine) and phenylamine.
Menaphthylamine	$C^{21}H^{17}N^{3}$	Chloride of cyanogen on naphtylamine.
Methylamine	$CH^{5}N$.	
Dimethylamine	$C^{2}H^{7}N$.	
Trimethylamine	$C^{3}H^{9}N$.	
Methyluramine	$C^{2}H^{7}N^{3}$.	Creatine or creatinine heated with oxide of mercury.
Metoluidine	$C^{15}H^{17}N^{3}$	Chloride of cyanogen on toluidine.
Morphine	$C^{17}H^{19}NO^{3}$	Opium.
Ethylmorphine	$C^{19}H^{23}NO^{3}$.	
Methylmorphine	$C^{18}H^{21}NO^{3}$.	
Naphtylamine	$C^{10}H^{9}N$	Reduction of nitronaphtylene.
Ethylnapthylamine	$C^{12}H^{13}N$.	
Nareeine	$C^{23}H^{29}NO^{9}$	Opium.
Narcotine	$C^{22}H^{23}NO^{7}$*	
Nicotine	$C^{10}H^{14}N^{2}$ or $C^{5}H^{7}N$	Tobacco.
Ninaphtylamine	$C^{10}H^{8}N^{2}O$	Reduction of dinitronaphtylene.
Octylamine	$C^{8}H^{19}N$	
Papaverine	$C^{20}H^{21}NO^{4}$	Opium.
Parvoline	$C^{9}H^{13}N$	Distillat. of bituminous shale of Dorsetshire.
Pelosine, or Cissampeline	$C^{18}H^{21}NO^{3}$	*Cissampelos pareira*, L. (Antilles).
Phenylamine	$C^{6}H^{7}N$.	Reduction of nitrobenzene, &c.
Amylphenylamine	$C^{11}H^{17}N$.	
Diamylphenylamine	$C^{16}H^{27}N$.	
Diethylphenylamine	$C^{10}H^{15}N$.	
Dicetylphenylamine	$C^{38}H^{71}N$.	
Cetylphenylamine	$C^{22}H^{39}N$.	
Ethylamylphenylamine	$C^{13}H^{21}N$.	
Ethylphenylamine	$C^{8}H^{11}N$.	
Methylamylphenylamine	$C^{12}H^{19}N$.	
Methylethylphenylamine	$C^{9}H^{13}N$.	
Methylphenylamine	$C^{7}H^{9}N$.	
Triphenylamine	$C^{18}H^{15}N$	Sulphite of cinnamyl-ammonium distilled with lime.
Vinylphenylamine (Phenylacetylamine	$C^{8}H^{9}N$. or $C^{16}H^{18}N^{2}$	
Phtalidine	$C^{8}H^{9}N$	Reduction of nitrophtalene.
Picoline	$C^{6}H^{7}N$	Coal-tar.
Piperidine	$C^{5}H^{11}N$	Piperine distilled with potash.
Amylpiperidine	$C^{10}H^{21}N$.	
Ethylpiperidine	$C^{7}H^{15}N$.	
Methylpiperidine	$C^{6}H^{13}N$.	
? Piperine	$C^{34}H^{38}N^{2}O^{6}$	Pepper (*Piper nigrum*, *P. longum*).
Propylamine. (See TRITYLAMINE.)		
Pyridine	$C^{5}H^{5}N$	Bone-oil.
Quinicine	$C^{20}H^{24}N^{2}O^{2}$	Isomeric transformation of quinine, or of quinidine.
Quinidine	$C^{20}H^{24}N^{2}O^{2}$	Cinchona bark.
Quinine	$C^{20}H^{24}N^{2}O^{2}$	
Ethylquinine	$C^{22}H^{28}N^{2}O^{2}$.	
Methylquinine	$C^{21}H^{26}N^{2}O^{2}$.	
Quinoleine	$C^{9}H^{7}N$	Quinine or Cinchonine distil. with potash.
Amylquinoleine	$C^{14}H^{17}N$.	
Ethylquinoleine	$C^{11}H^{11}N$.	
Methylquinoleine	$C^{10}H^{9}N$.	

* According to unpublished analyses by Matthiessen and Foster.

Name.	Formula.	Source or Mode of Formation.
Sarcine	$C^{5}H^{4}N^{4}O$	Juice of flesh.
Sarcosine	$C^{3}H^{7}NO^{2}$	Baryta-water on creatine.
Sinamine	$C^{4}H^{6}N^{2}$	Oxide of mercury on thiosinamine.
Ethylsinamine	$C^{6}H^{10}N^{2}$	Ethylthiosinamine heated with hydrate of lead.
Sinapine	$C^{16}H^{23}NO^{5}$	White mustard.
Sinapoline	$C^{7}H^{12}N^{2}O$	Hydrate of lead in oil of mustard (sulphocyanate of allyl).
Sincaline	$C^{5}H^{13}NO$	Alkalis on sinapine.
Sparteine	$C^{8}H^{13}N$	*Spartium scoparium*, L. (*Cytisus scoparius*, Linck.)
Strychnine	$C^{21}H^{22}N^{2}O^{2}$	*Strychnos nux vomica*, *S. Ignatii*, *S. colubrina.*
Tetrylamine (Petinine)	$C^{4}H^{11}N$	Bone-oil.
Thebaine	$C^{19}H^{21}NO^{3}$	Opium.
Theine. (See CAFEINE.)		
Theobromine	$C^{7}H^{8}N^{4}O^{2}$	Cacao-beans.
? Thiacetonine	$C^{9}H^{19}NS^{2}$	Ammonia and hydrosulphuric acid on acetone.
Thialdine	$C^{6}H^{13}NS^{2}$	Hydrosulphuric acid on aldehydammonia.
Thiosanime	$C^{4}H^{8}N^{2}S$	Ammonia on sulphocyanate of allyl (oil of mustard.)
Ethylthiosanimine	$C^{6}H^{12}N^{2}S$	Ethylamine on sulphocyanate of allyl.
Toluidine (Toluylamine)	$C^{7}H^{9}N$	Reduction of nitrotoluene.
Diethyltoluidine	$C^{11}H^{17}N.$	
Ethyltoluidine	$C^{9}H^{13}N.$	
Tritylamine	$C^{3}H^{9}N.$	
Urea (Carbamide	$CH^{4}N^{2}O.$	
Allylurea	$C^{4}H^{8}N^{2}O.$	
Amylurea	$C^{6}H^{14}N^{2}O.$	
Diallylurea. (See SINAPOLINE.)		
Diethylurea	$C^{5}H^{12}N^{2}O.$	
Diphenylurea. (See FLAVINE.)		
Ethylallylurea	$C^{6}H^{12}N^{2}O.$	
Ethylamylurea	$C^{8}H^{18}N^{2}O.$	
Ethylpiperylurea	$C^{8}H^{16}N^{2}O.$	
Ethylurea	$C^{3}H^{8}N^{2}O.$	
Methylethylurea	$C^{4}H^{10}N^{2}O.$	
Methylpiperylurea	$C^{7}H^{14}N^{2}O.$	
Methylurea	$C^{2}H^{6}N^{2}O.$	
Naphtylurea	$C^{11}H^{10}N^{2}O.$	
Phenylallylurea	$C^{10}H^{12}N^{2}O.$	
Phenylurea	$C^{7}H^{8}N^{2}O.$	
Piperylurea	$C^{6}H^{12}N^{2}O.$	
Sulphallylurea. (See THIOSINAMINE).		
Tolylurea	$C^{8}H^{10}N^{2}O.$	
Valeraldine	$C^{15}H^{31}NS^{2}$	Hydrosulphuric acid on valeral ammonia.
Veratrine	$C^{32}H^{52}N^{2}O$	*Veratrum album.*
?Vinylamine	$C^{2}H^{5}N$	Chloride of ethylene on ammonia.

2. Alkaloids comparable to hydrate of ammonium, forming salts by combining with acids and eliminating water.

Name.	Formula.
Amylium.	
Hydrate of Methyldiethylamylium	$C^{10}H^{25}NO.$
" Tetramylium	$C^{20}H^{45}NO.$
" Triethylamylium	$C^{11}H^{27}NO.$
Brucium.	
Hydrate of Ethylbrucium	$C^{25}H^{32}N^{2}O^{5}.$

Name.	Formula.
Conium.	
Hydrate of Diethylconium	$C^{12}H^{25}NO$.
„ Methylethylconium	$C^{11}H^{23}NO$.
Ethylenium.	
Hydrate of Trimethylethylenium	$C^{5}H^{15}NO$.
Ethylium.	
Hydrate of Methyltriethylium	$C^{7}H^{19}NO$.
„ Tetrethylium	$C^{8}H^{21}NO$.
Methylium.	
Hydrate of Tetramethylium	$C^{4}H^{13}NO$.
Nicotium.	
Hydrate of Ethylnicotium	$C^{7}H^{13}NO$.
„ Methylnicotium	$C^{6}H^{11}NO$.
Phenylium.	
Hydrate of Ethyltriphenylium	$C^{20}H^{21}NO$.
„ Methylethylamylophenylium	$C^{14}H^{25}NO$.
„ Triethylphenylium	$C^{12}H^{21}NO$.
Piperylium.	
Hydrate of Diethylpiperylium	$C^{9}H^{21}NO$.
Pyridine.	
Hydrate of Ethylpyridine	$C^{7}H^{11}NO$.
Strychnium.	
Hydrate of Amylstrychnium	$C^{26}H^{34}N^{2}O^{3}$.
„ Ethylstrychnium	$C^{23}H^{28}N^{2}O^{3}$.
Tolylium.	
Hydrate of Triethyltolylium	$C^{13}H^{23}NO$.

There are some substances not included in the above list, such as acetamide, $C^{2}H^{5}NO$, acetonitrile, $C^{2}H^{3}N$, &c., which possess the most important properties of alkaloids to quite as great an extent as some of the bodies there enumerated, but which, in most of their relations, are associated with other well defined groups of compounds, and are in consequence seldom classed among alkaloids. On the other hand, this list contains some bodies, such as urea and its derivatives, which also find their places in other classes, but which had long been regarded solely as alkaloids before their relations to other compounds were discovered. This inconsistency is unavoidable. There is not in nature any sharp distinction between alkaloids and other substances; hence, in determining whether particular bodies ought, or ought not, to be classed as alkaloids, we must sometimes decide by reference to customary usage, or other circumstances equally arbitrary.—G. C. F.

Alkaloids, detection of, in chemico-legal investigations. — The certain detection of the poisonous alkaloids in chemico-legal investigations involves their separation, in a state of purity, from the substances with which they are mixed. When, as is often the case, a very small quantity of an alkaloid is contained in a large quantity of a complicated mixture of animal or vegetable matter, its accurate separation is a problem of considerable difficulty. The first chemist who gave a systematic method of proceeding in such cases was Stas (Bulletin de l'Académie Royale de Médecine de Belgique, xi. 304 (1851); Ann. Ch. Pharm. lxxxiv. 379; J. Pharm. Chim. xxii. 281), and the method which he proposed continues to be the one most generally employed. His process consists in the successive and systematic use of various solvents, such as dilute acids, alcohol, and ether.

The method of carrying it out is as follows: When an alkaloid has to be sought for among the contents of the stomach or intestines, the substances to be examined are treated with twice their weight of pure absolute alcohol, to which from 0·5 gramme to 2 grammes of tartaric or oxalic acid (the former is preferable) have been added, and the mixture is heated in a flask to between 70° and 75° C. (When an entire organ, such as the liver, heart, or lungs, has to be examined for an alkaloid, it must first be divided as finely as possible, then moistened with pure absolute alcohol, squeezed, and afterwards washed with alcohol till all the soluble constituents are removed. The liquid thus obtained is treated in the same way as a mixture of suspected matter and alcohol.) When quite cold, the mixture is filtered, the insoluble part washed with strong alcohol, and the alcoholic solution evaporated either in vacuo, or in a rapid current of air at a temperature not exceeding 35° C.

If the residue left on evaporating the alcohol contains fat or other insoluble matter, it must be filtered again through a filter wetted with distilled water, the filtrate must be evaporated nearly to dryness in vacuo over sulphuric acid, and the residue exhausted with cold absolute alcohol. The alcoholic solution is once more evaporated at the atmospheric temperature, either in the air, or better in vacuo, and the acid residue of this evaporation is dissolved in the *smallest possible* quantity of water. To the solution so obtained, pure, powdered acid carbonate of potassium or of sodium is added *very gradually* until there is no more effervescence. The neutralised solution is shaken with from four to five times its bulk of *pure* ether, and then allowed to settle. When the layer of ether has become perfectly clear, a little of it is decanted into a glass capsule, and left to spontaneous evaporation in a very dry place. If, after the evaporation of the ether, slight streaks of liquid appear on the side of the capsule, and run together slowly to the bottom of it, a liquid and volatile alkaloid is probably present. If this be the case, the warmth of the hand will be sufficient to cause the contents of the capsule to exhale a disagreeable smell which, according to the nature of the alkaloid, is more or less sharp, choking, and irritating. If these indications are wanting, the alkaloid, if any is present, is probably solid and non-volatile. According to the nature of the alkaloid, as indicated by this preliminary trial, Stas recommends different processes for its further purification.

A. *The alkaloid is liquid and volatile.*—In this case 1 or 2 cub. cent. of strong solution of caustic potash or soda are added to the contents of the flask, from which the small quantity of the ethereal solution was taken, and the whole is again well shaken. After standing for a sufficient time, the ether is poured off, and the residue is again shaken three or four times with fresh quantities of ether. The ethereal liquids so obtained, containing the alkaloid in solution, are united and shaken with 1 or 2 cub. cent. of a mixture of 4 parts by weight of water and 1 part of sulphuric acid; after being allowed to stand, the ether is poured off, and the acid liquid is washed with a second quantity of ether.

As the sulphates of the volatile alkaloids are soluble in water, but almost all insoluble in ether, the alkaloid sought is contained in the dilute sulphuric acid, in the form of pure sulphate [*], while the animal matter which the ether may have taken up from the alkaline liquid together with the alkaloid, remains still dissolved by it.

In order to obtain the alkaloid from the solution of its sulphate, the latter is mixed with a strong solution of caustic potash or soda; the mixture is well shaken, and then exhausted with pure ether, which dissolves the alkaloid together with ammonia. The ethereal solution is allowed to evaporate [†] at as low a temperature as possible, and in order to remove from the residue the last traces of ammonia, the vessel containing it is placed for an instant in vacuo over sulphuric acid. The alkaloid then remains in a state of purity, with its characteristic chemical and physical properties.

B. *The alkaloid is solid and fixed.*—If on evaporating a small quantity of the ether with which the liquid neutralised by acid carbonate of sodium has been mixed (see above), there is no sign of the presence of a volatile alkaloid, the liquid must be further examined for fixed alkaloids as follows. Caustic potash or soda is put into the flask containing ether and the neutralised solution, the mixture is again vigorously shaken, the ethereal layer is poured off as soon as it is clear, and the watery alkaline liquid is several times washed with a considerable quantity of fresh ether. The ether now contains the free alkaloid in solution [‡], and on evaporation leaves either a solid residue or a colourless milky liquid containing solid particles in suspension. The smell of this residue is disagreeably animal, but not sharp; it colours red litmus-paper permanently blue.

In order to obtain the alkaloid in the crystalline state, a few drops of alcohol are poured into the capsule containing it and allowed to evaporate. Usually, however, it is still too impure to crystallise in this way. When this is the case, a few drops of water made very slightly acid by sulphuric acid, are poured upon the residue left by the evaporation of the alcohol, and made to come in contact with the whole of it by properly inclining the capsule in various directions: the alkaloid is thus dissolved, while the fatty impurities remain adhering to the capsule. The acid solution, which, if the last operation has been well performed, is clear and colourless, is poured off, the capsule is washed with a few drops more of the acid water, the washings are mixed with the first solution, and the whole is evaporated over sulphuric acid to about three quarters of its bulk. A saturated solution of pure carbonate of potassium

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[*] Sulphate of *conine* being not quite insoluble in ether, a little of this alkaloid may remain in the ethereal solution; the greater part, however, is always in the aqueous acid solution.

[†] If *conine* be present, a great part of it will evaporate with the ether.

[‡] If *morphine* has to be sought for the liquid should be shaken with ether *immediately* after being neutralised with carbonate of sodium, and the ether should be poured off as quickly as possible, for, if the alkaloid have time to separate in the crystalline form, scarcely any of it is dissolved by the ether. (Otto.)

is added to the remaining liquid, and the mixture is treated with absolute alcohol, which dissolves the liberated alkaloid, but leaves undissolved the sulphate and excess of carbonate of potassium. On evaporating the alcoholic solution, the alkaloid is obtained crystallised, and in a state to show its characteristic reactions.

According to Otto (Ann. Ch. Pharm. c. 39) the above process of purifying the fixed alkaloids may be advantageously modified as follows. Instead of decomposing the impure tartrate or oxalate by acid carbonate of potassium or sodium, and obtaining a solution of the free alkaloid in ether, as described in the first part of this article, the salt dissolved in a small quantity of water is washed with ether, as long as the ether is coloured by it and leaves a residue on evaporation, and *afterwards* the solution is neutralised by carbonate of sodium and ether added to dissolve the alkaloid as already described. On evaporating the ethereal solution thus prepared, the alkaloid is left in a state of great purity. Or, the acid sulphate of the alkaloid may be formed and washed with ether, as in the process for purifying a volatile alkaloid.

Another method of detecting and separating the organic alkaloids from mixtures of other substances has been given by Sonnenschein (Ann. Ch. Pharm. civ. 45). This method is founded upon the property which the alkaloids possess, in common with ammonia, of giving precipitates in an acid solution of *phosphomolybdate* of *sodium*: it is very easy of execution, and seems to give very accurate results.

Phosphomolybdate of sodium is thus prepared. The yellow precipitate obtained by mixing acid solutions of molybdate of ammonium and phosphate of sodium is well washed, suspended in water, and heated with carbonate of sodium till it is completely dissolved. The solution is evaporated to dryness, and the residue ignited till all ammonia is expelled: if any reduction of molybdic acid take place during the ignition, the product is moistened with nitric acid and again ignited. It is then heated with water, nitric acid added till the solution has a strongly acid reaction, and the gold-yellow solution thus obtained is diluted till 10 parts of the solution contain 1 part of solid residue. It must be carefully preserved from contact with ammonia.

This reagent is applied to the separation of the alkaloids in the following manner. The whole of the organic matter to be examined is repeatedly exhausted with very dilute hydrochloric acid: the extract is evaporated at a heat of 30° C. to the consistence of a thin syrup, then diluted, and left for some hours in a cool place before filtration. The filtrate is precipitated by excess of phosphomolybdic acid, the precipitate collected on a filter, thoroughly washed with water containing phosphomolybdic and nitric acids, and introduced while moist into a flask. Caustic baryta is added, to a distinct alkaline reaction: and the flask having been fitted with a delivery-tube which is connected with a bulb-apparatus containing hydrochloric acid, heat is gradually applied, when the ammonia and volatile organic bases distil over, and are collected in the hydrochloric acid. The residue in the flask (containing the non-volatile alkaloids) is freed from excess of baryta by a current of carbonic anhydride, carefully evaporated to dryness, and extracted with strong alcohol. On evaporating the alcoholic solution, the bases are commonly obtained in a state of such purity that they will at once exhibit their characteristic reactions: occasionally, however, they require to be further purified by recrystallisation from alcohol or ether.

A process has been employed by Graham and Hofmann (Chem. Soc. Qu. J. v. 173; Ann. Ch. Pharm. lxxxiii. 39; Pharm. J. Trans. xi. 504) for the detection of strychnine in beer, which might doubtless be employed with equal advantage for the detection of other alkaloids in large quantities of liquid. It consists in leaving the liquid to be examined in contact with about a fortieth of its weight of good animal charcoal for a day, the whole being frequently shaken, collecting the charcoal on a filter, washing it once or twice with water, and then boiling it for half an hour with alcohol, which dissolves out the alkaloid. The alcoholic solution is evaporated, the residue is made alkaline by the addition of a few drops of potash or soda, and then shaken up with ether, which, when poured off and evaporated, leaves the organic base with its characteristic properties.

Schulze (Ann. Ch. Pharm. cix. 177) has indicated the acid liquid obtained by dropping pentachloride of antimony into aqueous phosphoric acid as a very delicate reagent for certain alkaloids, and as a substance which may probably serve for the separation of the alkaloids in general.

When an alkaloid has been separated in a state of purity by one of the above processes, or by any other, its chemical and physical properties must be carefully observed in order to determine its individual character, and the reactions obtained should in every case be controlled by comparison with those given by a pure specimen of the substance suspected.

From what has been stated above relative to the absorption of the alkaloids by animal charcoal, it is evident that that substance should never be employed to decolorise a solution previous to its being examined for poisonous organic bases. The employment of basic acetate of lead for the same purpose should also be avoided, since it not only introduces a poisonous metal into the substance to be examined, but the sulphuretted hydrogen, which is required to remove the lead, is apt to combine with some of the organic matters present, forming compounds which, in contact with the air, give rise to highly coloured and disagreeably smelling products, very difficult afterwards to get rid of. (Stas.)

For further details concerning modifications of Stas's process, and for some methods which are not mentioned in this article, the reader is referred to the article on the same subject in Liebig, Poggendorff, and Wöhler's "Handworterbuch der reinen und angewandten Chemie," 2nd edition, i. 464; and for the reactions of the individual alkaloids, to the various articles in this Dictionary in which they are specially described.—G. C. F.

ALKANET. The commercial name of two different plants. *True alkanet* consists of the leaves and roots of the *Lawsonia inermis*, which grows wild in the Levant. The leaves pulverised and made into a paste with water yield a yellow dye. The root, which contains a red pigment, is used as a cosmetic.

False alkanet (*Orcanette, Radix alcannæ spuriæ*) is the root of *Anchusa tinctoria*, which grows in France, Spain, Italy, Hungary and Greece. It is inodorous, has a faint, somewhat astringent taste, and colours the saliva. It is used in dyeing to produce a very brilliant violet and a grey; and for this purpose, linen or cotton goods previously prepared with alum-mordants for violet, and with iron-mordants for grey, are dipped in an alcoholic extract of the root. It is also used for dyeing silk, but not for wool. The colouring matter is called *Anchusin* (which see).

ALKARGEN and **ALKARSIN.** (See ARSENIDES OF METHYL.)

ALLAGITE. A mineral which appears to be an intimate mixture of hornstone and silicate of manganese, perhaps also with carbonate of manganese.

ALLAITE. Syn. of DIOPSIDE and AUGITE.

ALLANITE. (See ORTHITE.)

ALLANTOIC and **AMNIOTIC LIQUIDS.** The fœtus of most mammiferous animals is enveloped in two membranes, the outer of which is called the *allantois*, and the inner the *amnium*. The space between the two is connected by a duct with the urinary bladder of the fœtus, and contains a liquid called the allantoic liquid, which is in fact the urine of the fœtus. The amnium at first lies close upon the fœtus, but gradually separates and becomes filled with a liquid in which the fœtus floats suspended by the umbilical cord. This liquor is the *liquor amnii.*

The allantoic liquid is especially distinguished by containing allantoin, together with albumin, alkaline lactates, chloride of sodium and phosphates, and sometimes glucose. The amniotic liquid contains albumin, pyin, a substance resembling mucus, extractive matter, and in some instances glucose, together with alkaline chlorides, sulphates and phosphates.

These liquids have been investigated by many distinguished chemists, but the most exact analyses of them are those which have been recently made by Schlossberger (Ann. Ch. Pharm. xcvi. 67, and ciii. 193), and by Majewski (Dissert. de Substantiarum, &c., Dorpat, 1858; J. pr. Chem. lxxvi. 99). Majewski's results are as follows:

Both liquids, in the earlier stages of development of the embryo of cows and sheep, are clear and colourless: at a later stage, the amniotic liquid of the cow becomes gummy and yellowish, also turbid; in sheep and swine on the contrary, it always remains clear and colourless, and never becomes gummy. The allantoic liquid becomes yellower with age, and at last reddish yellow, but remains clear, excepting in swine, in which it is always turbid. Both liquids generally exhibit an alkaline reaction.

In both liquids, the solid constituents, organic and inorganic, increase for the most part in quantity as the development of the fœtus progresses. In the human fœtus, however, the quantity of solid matter in the amniotic liquid decreases considerably towards the time of birth (see table). The same result was obtained by Vogt and by Scherer, the latter of whom found 2·416 per cent. of solid constituents in the amniotic liquid in the fifth month of gestation, and only 0·852 at birth.

The amniotic liquid retains its albumin up to the period of maturity of the fœtus, but (as appears from investigations on the human embryo) this amount decreases in the later period of the development of the embryo, and this diminution appears to be connected with the formation of the placenta. In the amniotic liquid of the cow, the albumin may be recognised by its ordinary properties in the earlier stages of development, but afterwards the liquid becomes gummy and no longer exhibits the usual reaction with nitric acid. The same result was obtained by Schlossberger, (p. 130).

The allantoic liquid increases in quantity and consistence as the development of the embryo advances; it is always clear (excepting in swine) and resembles saturated urine. The allantoic liquid of swine contains iron and a peculiar compound of lime and albumin.

In both liquids, the quantity of sugar gradually increases from the earliest period of fœtal life, and is greatest a short time before birth. Sugar appears however to be present only in the vegetable feeders: in human embryonic liquids it cannot be detected.

The quantity of inorganic salts increases as development advances. Both liquids contain chlorides, phosphates and sulphates, the quantity being greater in the allantoic than in the amniotic liquid.

The following table exhibits a summary of the quantitative results obtained by Majewski:

	Period of Development.		Quantity in cub. cent.	Spec. grav.	In 100 parts.								
					Water.	Solid substance.	Organic.	Inorganic.	Albumin.	Sugar.	Urea.	P^2O^5	SO^3
Embryo of Sheep.	Week 3—4	Amnios											
		Allantois	27	1·0029	99·357	0·643	0·459	0·184		0·243			
	„ 4—6½	Amnios	19	1·0018	99·460	0·540	0·400	0·140	0·105	0·063	0·20		
		Allantois	63	1·0065	98·980	1·020	0·650	0·370		0·241	0·40	0·0047	0·0052
	„ 6½—9	Amnios	62	1·0017	98·945	1·055	0·685	0·370	0 125	0·114	0·302	0·0078	0·0061
		Allantois	59	1·0082	98·127	1·873	1·198	0·675		0·449	0·500	0·0356	0·0069
	„ 10—12½	Amnios	163	1·0069	98·515	1·485	0·917	0·568	0·170	0·172	0·370	0·0148	0·0034
		Allantois	119	1·0104	97·453	2·547	1·671	0·876		0·642	0 606	0·0137	0·0475
	„ 12½—18	Amnios	657	1·0064	98·660	1·340	0·905	0·435	0·241	0·196	0·475	0·0827	0·006
		Allantois	336	1·0097	97·380	2·620	0·960	0·660		0·667	0·780	0·0898	0·0326
Embryo of Cow.	„ 9—12	Amnios	675	1·0047	98·970	1·03	0·600	0·430	0·032	0·101	0·200	0·018	0·009
		Allantois	95	1·010.	97·310	2·69	1·800	0·890		0·555	0·330	0·060	0·033
	„ 12—22	Amnios	1624	1·0064	98·554	1·446	0·876	0 570	0·097	0·191	0·298	0·031	0·022
		Allantois	613	1·0125	96·858	3·142	2·338	0·804		0·605	0·645	0·022	0·097
	„ 21—27	Amnios	698	1·0075	98·076	1·924	1·171	0·753	0·215	0·302	0·426	0·016	0·022
		Allantois	1236	1·0165	96·160	3·840	2·767	1·073		0·642	0·657	0·038	0·112
Human Embryo.	In the 2nd month	Amnios			95·405	5·595			2·288	none			
	At birth . .	„		1·0049	98·490	1·510	0·95	5·600	0·357	none	0·380		
Embryo of Swine	Between six and eight weeks	Amnios	60	1·0064	98·114	1·886	1·248	0·638	0·562	trace	0·240		
		Allantois	18	1·0088	97·580	2·420	1·705	0·715		trace	0·358		

Schlossberger found in the embryonic liquid of cows the following quantities of water and inorganic salts: — The ages of the fœtus were: of (*a*) 30 weeks; (*b*) 18 weeks; (*c*) 15 weeks; (*d*) 7—8 weeks; (*e*) 5 weeks, and (*f*) 3 weeks:

		Water.	Ash.	Soluble Salts.	Insoluble Salts.
Amniotic liquid.	*a.*	97·18			
	b.	97·28	0·72	0·694	0·026
	c.	98·96	1·02	1·00	0·02
	d.	98·67			
	e.		0·89	0·86	0·03
	f.	98·12			
Allantoic liquid.	*c.*	97·33	0·93	0·91	0·02
	e	98·76	0·73	0·70	0·03
	f.	97·35	0·71		

The liquids, even in the fresh state, exhibited an alkaline reaction, and effervesced briskly with acids: and they all exhibited the reactions of sugar, the amniotic liquid of *d* containing 0·092 per cent. of that substance, and the allantoic liquid of the same, 0·454 per cent. Schlossberger did not find urea in the amniotic liquid.

The albuminoïdal substances of both liquids exhibited differences of character amongst themselves, and many unusual reactions, indicating the presence of compounds intermediate between albumin casein, mucus and pyin. The reactions observed by Schlossberger are given in the following table:

	Amniotic liquid of *a* and *c*.	Allantoic liquid of *b* and *c*.
Appearance. Reaction on boiling and on addition of acetic acid.	*a.* Viscid like white of egg: mixed easily with water, and filtered readily. On boiling, became more mobile, with scarcely perceptible turbidity. On neutralising with acetic acid: scarcely perceptible turbidity, the liquid remaining viscid. On boiling, small flocks separated. The greater part of the protein-substance remained dissolved. On evaporation: films. *b.* Not viscid. Remained perfectly clear when boiled, either alone or with acetic acid.	*b.* Not viscid; clear on boiling. Acetic acid produces slight turbidity, and redissolves the flocks but slowly, even in excess and at the boiling heat. *c.* Coagulates even when boiled alone, the coagulum being but partially soluble in acetic acid. On evaporation: films. Both *b* and *c* become very turbid when boiled with chloride of calcium or sulphate of magnesium, especially *c*. The turbidity (arising in *b* most probably from carbonates) disappears on adding acetic acid.
Alcohol.	*a.* Throws down flocks soluble in warm water. *c.* No change.	*b.* No change. *c.* Turbidity.
Nitric acid.	*a.* Slight turbidity, disappearing with excess of acid. *c.* No turbidity. Liquid does not become yellow on boiling.	*b.* Scarcely perceptible turbidity. *c.* Precipitate and yellow colour on boiling.
HgCl.	*a.* Slight turbidity: small flakes on boiling. *c.* Turbidity. (With NO^6Hg: copious precipitate).	*b.* No change. *c.* Precipitate.
Ferrocyanide of potassium.	*a.* No change. *c.* Turbidity only after addition of acetic acid.	*b.* No change. *c.* After acidulation: flocks.
Acetate of lead. Basic acetate of lead. Tannin.	Copious precipitates.	Copious precipitates.
Alum.	No change in any instance.	

ALLANTOIN. $C^4H^6N^4O^3$, or $C^8H^6N^4O^6$.—Discovered by Vauquelin and Buniva (Ann. Chim. xxxiii. 269) in the amniotic liquid of the cow.* Lassaigne (Ann. Ch. Phys. [2] xvii. 301) obtained it from the allantoic liquid of the cow, and Wöhler (Ann. Ch. Pharm. lxx. 220) from the urine of calves. It is formed artificially by treating uric acid with water and peroxide of lead. (Liebig and Wöhler, Ann. Ch. Pharm. xxvi. 244.)

$$\underbrace{C^5H^4N^4O^3}_{\text{Uric acid.}} + H^2O + 2PbO = \underbrace{C^4H^6N^4O^3}_{\text{Allantoin.}} + \underbrace{CPb^2O^3}_{\text{Carbonate of lead.}};$$

or with a mixture of ferricyanide of potassium and caustic potash. (Schlieper, Ann. Ch. Pharm. lxvii. 216.)

$$\underbrace{C^5H^4N^4O^3}_{\text{Uric acid.}} + \underbrace{2C^6N^6Fe^2K^3}_{\text{Ferricyanide of potassium.}} + 4KHO = \underbrace{C^4H^6N^4O^3}_{\text{Allantoin.}} + \underbrace{CK^2O^3}_{\text{Carbonate of potassium.}} + \underbrace{4C^3N^3FeK^2}_{\text{Ferrocyanide of potassium.}} + H^2O.$$

Preparation.—Pulverised uric acid is suspended in water, nearly at the boiling heat, and finely pounded oxide of lead is added by small portions, and with frequent stirring, till the last portions no longer turn white. The liquid filtered while hot deposits on

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* As, however, subsequent experimenters have not been able to obtain it from that source, it is probable that the amniotic liquid was mixed with allantoic liquid.

cooling, crystals of allantoin, while urea remains in solution, and oxalate of lead is left on the filter. The two latter compounds are produced by the action of the excess of peroxide of lead on the allantoin. (Liebig and Wöhler.)

$$C^4H^6N^4O^3 + 2PbO + H^2O = \underbrace{2CH^4N^2O}_{\text{Urea.}} + \underbrace{C^2Pb^2O^4}_{\text{Oxalate of lead.}}$$

To obtain allantoin from the allantoic liquid, the liquid is evaporated to a fourth of its bulk, and the crystals which are deposited on cooling are decolorised with animal charcoal. From calves' urine, it is prepared by evaporating the liquid to a syrup, and leaving it at least for several days, then diluting with water; washing the deposit with water to separate a quantity of gelatinous matter, chiefly consisting of urate of magnesium; boiling the crystalline residue of allantoin and phosphate of magnesium with water and animal charcoal; filtering at the boiling heat; and adding a few drops of hydrochloric acid to the filtrate to retain in solution the small quantity of phosphate of magnesium dissolved in the boiling liquid. The allantoin is then deposited in crystals on cooling.

Properties.—Allantoin forms shining colourless prisms, having a vitreous aspect, and belonging, according to Dauber (Ann. Ch. Pharm. lxxi. 68), to the monoclinic system. It is tasteless and without action on vegetable colours. It dissolves in 160 pts. of water at 20° C., and in 30 pts. of boiling water. Alcohol dissolves it in larger quantity.

Decompositions.—By dry distillation, allantoin is resolved into carbonate and cyanide of ammonium, a small quantity of empyreumatic oil and a very porous charcoal. When gently heated with nitric or hydrochloric acid, it is converted into urea and allanturic acid. (Pelouze, Gerhardt.)

$$C^4H^6N^4O^3 + H^2O = CH^4N^2O + \underbrace{C^3H^4N^2O^3}_{\text{Allanturic acid.}}$$

Heated with *sulphuric acid*, it is resolved into carbonic acid, carbonic oxide, and ammonia. (Liebig and Wöhler.)

$$C^4H^6N^4O^3 + 3H^2O = 2CO^2 + 2CO + 4NH^3.$$

Boiled with *baryta water*, it gives off ammonia and precipitates oxalate of barium:

$$C^4H^6N^4O^3 + 4BaHO + H^2O = 4NH^3 + 2C^2Ba^2O^4.$$

Similarly with aqueous *potash* (Liebig and Wöhler). A solution of allantoin in cold potash deposits all the allantoin unaltered, if immediately mixed with acids; but in the course of a day or two, it changes spontaneously into *hydantoate of potassium* ($C^4H^7KN^4O^4$), and is then no longer precipitated by acids, gives off but little ammonia when boiled, and does not form any oxalic acid:

$$C^4H^6N^4O^3 + KHO = C^4H^7KN^4O^4;$$

by the further action of the alkali, the hydantoate of potassium is resolved into urea and lantanurate of potassium:

$$C^4H^7KN^4O^4 = CH^4N^2O + C^3H^3KN^2O^3.$$

When the aqueous solution of allantoin is boiled with *metallic oxides*, compounds are formed which may be called *salts of allantoin*. Some of them consist simply of allantoin in which 1 at. H is replaced by a metal; thus, the *cadmium*-compound is $C^4H^5CdN^4O^3$: and the *silver*-compound, obtained by mixing a solution of allantoin with nitrate of silver and then with ammonia, is $C^4H^5AgN^4O^3$. But most of them contain an excess of the metallic oxide; thus, the zinc-compound is $Zn^2O.2C^4H^5ZnN^4O^3$, and the lead-compound $Pb^2O.4C^4H^5PbN^4O^3$. These compounds are insoluble or sparingly soluble in water, and decompose at 100° or a little above (Limpricht, Ann. Ch. Pharm. lxxxviii. 94). The silver-compound was obtained by Liebig and Wöhler.

When a solution of allantoin is boiled with excess of mercuric oxide, the filtrate becomes milky on cooling, and after a while deposits an amorphous powder containing $Hg^2O.3C^4H^5HgN^4O^3$, or $5HgO.3C^8H^5N^4O^5$. Three other compounds are said to be obtained from the mother-liquor. Allantoin does not precipitate corrosive sublimate; but with mercuric nitrate, in a cold and very dilute solution, it forms a precipitate containing $3Hg^2O.4C^4H^5HgN^4O^3$, or $5HgO.2C^8H^5N^4O^6$.

On this last property is founded a method for the quantitative estimation of allantoin, by precipitation with a graduated solution of mercuric nitrate. The method is similar to Liebig's process for the estimation of urea (*q. v.*), but is applicable to the estimation of allantoin only in liquids not containing urea. To precipitate 100 grms. of dry allantoin, $C^4H^6N^4O^3$, requires 172 grms. of mercuric oxide: consequently 10 cub. cent. of a graduated solution of mercuric nitrate containing 0·770 grm.

mercuric oxide, will precipitate 0·448 grm. allantoin. The liquid should contain a considerable excess of the mercuric salt.

ALLANTURIC ACID. $C^3H^4N^2O^3$.—A product of the decomposition of allantoin under the influence of nitric acid, hydrochloric acid, or peroxide of lead (p. 131): also obtained by treating uric acid with nitric acid or chlorine. It is a white solid body, slightly acid, deliquescent, nearly insoluble in alcohol, and yields by distillation a product containing hydrocyanic acid, with a bulky residue of charcoal. With nitrate of silver and acetate of lead, it forms white bulky precipitates, soluble in excess of these salts, and of allanturic acid. (Pelouze, Ann. Ch. Phys. [3] vi. 71.)

ALLEMONTITE. Arsenide of Antimony. (p. 371.)

ALLITURIC ACID. $C^3H^3N^2O^2$? Obtained by mixing an aqueous solution of alloxantin with excess of hydrochloric acid, boiling the liquid rapidly down to a small quantity, treating the pulverulent mixture of alliturie acid and undecomposed alloxantin with nitric acid to dissolve out the latter, and dissolving the residue in 15 or 20 pts. of hot water. The solution on cooling deposits alliturie acid in the form of a bulky yellowish white powder. It dissolves in strong sulphuric acid, and is precipitated from the solution by water. Its solution in ammonia yields *allliturate of ammonium*, by spontaneous evaporation, in colourless shining needles. The acid is decomposed by boiling with potash, with evolution of ammonia. (Schlieper, Ann. Ch. Pharm. lvi. 20.)

ALLIUM SATIVUM. (*Garlic.*) 100 pts. of the ash of the fresh plant yield 0·54 p.c. ash, containing in 100 parts: 12·17 carbonic anhydride, 4·82 sulphuric anhydride, 2·18 phosphoric anhydride, 35·13 potash, a trace of soda, 2·75 chloride of sodium, 5·74 carbonate of calcium, 6·89 carbonate of magnesium, 30·09 basic phosphate of calcium, 0·22 silica, and traces of the phosphates of magnesium and iron.

ALLOCHROÏTE. A variety of garnet, fine-grained, massive, and of dark dingy colour. (See GARNET.)

ALLOGONITE. Syn. with HERDERITE.

ALLOMORPHITE. Breithaupt's name for a mineral from Rudolstadt, which, according to the analysis of Gerngross, appears to be merely sulphate of barium.

ALLOPHANE. A hydrated silicate of aluminium, of a blue and sometimes green or brown colour, occurring massive, or in imitative shapes, in a bed of iron-shot limestone, or greywacke slate in the forest of Thuringia. It is transparent or translucent on the edges, moderately hard, but very brittle. Fracture imperfectly conchoidal. Lustre vitreous. Specific gravity 1·89. According to Stromeyer's analysis, it contains 21·92 silver, 32·2 alumina, 3·06 ferric hydrate, 0·73 lime, 0·52 sulphate of calcium, 3·06 carbonate of copper, and 41·30 water. Bunsen found in a specimen from a bed of lignite near Bonn, nearly the same composition, with a slight admixture of the carbonates of calcium and magnesium, but no copper. The mineral appears from the analyses of Walchner, Berthier, Guillemin, and others, to vary considerably in composition, but irrespective of foreign admixtures it agrees nearly with the formula $Al^4O^3.3SiO^2 + 5H^2O$. Schnabel (Jahresber. d. Chem. 1850, s. 731), has, however, analysed several allophanes containing from 14 to 19 per cent. of oxide of copper.

ALLOPHANIC ACID. $C^2H^4N^2O^3 = \left.\begin{matrix}C^2H^3N^2O^2\\ H\end{matrix}\right\}O$. *Ureo-carbonic acid.* (Gm. ix. 266; Gerh. i. 418.) By passing the vapour of cyanic acid into absolute alcohol, Liebig and Wöhler obtained in 1830 a peculiar ether, which they regarded as cyanate of ethyl; but in 1847 (Ann. Ch. Pharm. lix. 291), they discovered that the substance thus formed was the ether of a peculiar acid which they called allophanic acid.

This acid contains the elements of 2 at. cyanic acid and 1 at. water:

$$C^2H^4N^2O^3 = 2CHNO + H^2O.$$

Its ethers are produced when the vapour of cyanic acid comes in contact with the corresponding alcohols, and these ethers, treated with caustic alkalis, yield the corresponding salts of allophanic acid. The acid itself is not known in the separate state; when its salts are decomposed by a stronger acid, it is resolved into carbonic anhydride and urea:

$$C^2H^4N^2O^3 = CO^2 + CH^4N^2O.$$

In like manner the salts when heated in the state of aqueous solution, are resolved into carbonic anhydride, a carbonate, and urea.

Allophanate of Barium.—Obtained by dissolving allophanate of methyl or ethyl in baryta-water, whereby wood-spirit or alcohol is set free. The best method is to triturate allophanate of ethyl with crystals of hydrate of barium and baryta-water, without applying heat, till the ether disappears; filter from the remaining baryta-crystals; and set aside the filtrate for some days in a closed vessel; the barium-salt then separates gradually in hard crystalline nodules and crusts. The crystals are separated from the vessel under the liquid; the liquid quickly decanted; any carbonate of barium that may have been formed, is separated by elutriation; and the crystals are washed a few times with a small quantity of cold water, and dried on paper at the temperature of the air.

The barium-salt has an alkaline reaction. When heated alone, it does not give off a trace of water, but evolves monocarbonate of ammonium, and leaves cyanate of barium. Its aqueous solution becomes turbid below 100° C., gives off carbonic anhydride with effervescence, deposits all the baryta in the form of carbonate, and afterwards contains nothing but urea in solution:

$$2C^2H^3BaN^2O^3 + H^2O = CO^3Ba^2 + CO^2 + 2CH^4N^2O.$$

This salt, when an acid is poured upon it, is decomposed with brisk effervescence, yielding carbonic anhydride and urea; even carbonic acid produces this decomposition, though slowly; neither cyanic acid nor ammonia is formed.

Allophanate of Calcium.—Prepared like the barium-salt. Crystallisable. Sparingly soluble in water.

Allophanate of Potassium.—A solution of allophanic ether in alcoholic potash quickly deposits this salt in laminæ resembling those of chlorate of potassium.

Allophanate of Sodium.—Obtained like the potassium-salt, or by triturating the barium-salt, without application of heat, with an equivalent quantity of aqueous sulphate of sodium, and pouring alcohol upon the filtrate, which causes the sodium-salt to crystallise out in small prisms having an alkaline reaction. The aqueous solution of the salt evaporated without heat in vacuo, leaves the salt in the form of an iridescent gelatinous mass; evaporated between 40° and 50° C. it leaves the salt partly undecomposed, partly resolved into urea and carbonate of sodium. The aqueous solution mixed with nitric acid gives off carbonic anhydride and deposits shining scales of nitrate of urea. It does not precipitate chloride of barium, in the cold, but, when heated with it, forms an immediate precipitate of carbonate of barium.

Allophanic Ethers.—These compounds contain the elements of 2 at. cyanic acid, and 1 at. of an alcohol, monatomic, diatomic, or triatomic, *e. g.*

Allophanate of Ethyl . . . $C^4H^8N^2O^3 = 2CNHO + C^2H^6O$
Allophanate of Ethylene . . $C^4H^8N^2O^4 = 2CNHO + C^2H^6O^2$
Allophanate of Glyceryl . . $C^5H^{10}N^2O^5 = 2CNHO + C^3H^8O^3$

They are obtained by passing the vapour of cyanic acid into the alcohols.

Allophanate of Amyl, $C^7H^{14}N^2O^3 = C^2H^3(C^5H^{11})NO^3$.—Amylic alcohol rapidly absorbs the vapours produced by the action of heat on cyanuric acid, the liquid, after a while, solidifying into a magma of crystals, which may be purified by solution in boiling water. (Schlieper, Ann. Ch. Pharm. lix. 23.)

Allophanate of amyl forms nacreous scales, unctuous to the touch, and without taste or odour. It is insoluble in cold water, and its solution in hot water is neutral to vegetable colours, and does not precipitate metallic salts. It is very soluble in alcohol and in ether, and is precipitated from the solutions by water. It is not attacked by chlorine, bromine, nitric acid, or hydrosulphuric acid. It melts at a gentle heat, and sublimes without alteration; but its melting-point is very near that at which decomposition takes place. When heated above 100° C. it boils, gives off vapours of amylic alcohol, and leaves a residue of cyanuric acid, $3C^7H^{14}N^2O^3 = 3C^5H^{12}O + 2C^3N^3H^3O^3$. Distilled with fixed alkalis, it gives off amyl-alcohol (Schlieper). According to Wurtz (Compt. rend. xxix. 186), hot potash-ley converts it into carbonate of potassium, amylamine, and ammonia:

$$C^7H^{14}N^2O^3 + 4KHO = 2CO^3K^2 + C^5H^{13}N + NH^3 + H^2O.$$

Allophanate of Ethyl, or *Allophanic Ether*, $C^4H^8N^2O^3 = C^2H^3(C^2H^5)N^2O^3$.—When the vapours evolved from heated cyanuric acid are passed into absolute alcohol, the liquid becomes very hot and gradually deposits crystals of allophanic ether. The product is washed with a small quantity of alcohol, then dissolved in a mixture of alcohol and ether, and left to crystallise by evaporation (Liebig and Wöhler, Ann. Ch. Pharm. lviii. 260; lix. 291). According to Debus, allophanic ether is likewise produced by the action of ammonia on dicarbonate of ethylic disulphide.

Allophanic ether crystallises in colourless transparent needles, having a strong lustre. It is insoluble in cold water, but dissolves in boiling water and in alcohol, sparingly in ether. The solutions are neutral to test-papers, have no taste, and do not precipitate metallic salts.

The ether dissolves in ammonia somewhat more freely than in water, and crystallises therefrom, apparently free from ammonia. It dissolves in dilute sulphuric and nitric acid at the boiling heat, apparently without decomposition.

The crystals when heated in an open vessel melt and volatilise, the vapours condensing in the air in woolly flocks.

Treated with cold alcoholic potash or baryta-water, it yields a metallic allophanate and alcohol; with a boiling solution of potash, it forms cyanurate of potassium.

Allophanate of Ethylene, $C^4H^8N^2O^4 = \left.\begin{matrix}C^2H^3N^2O^2\\ H.C^2H^4\end{matrix}\right\}O^2$. *Allophanate of Glycol.*—Glycol (hydrate of ethylene) absorbs cyanic acid vapour with considerable force, so that it is best to cool the liquid during the absorption. The product is a white mass which dissolves in boiling alcohol, and separates on cooling in colourless shining laminæ. It is soluble in water, and melts at 100° C. without decomposition, to a clear colourless liquid, which solidifies in the crystalline form on cooling. At a stronger heat, it gives off carbonate of ammonium, and a thick viscid liquid, while cyanuric acid remains behind. Strong acids decompose it. With hydrate of barium, it behaves like the glycerin-compound next to be described; also with alcoholic potash. Strong aqueous potash likewise decomposes it, without formation of cyanuric acid. (Baeyer, Ann. Ch. Pharm. cxiv. 160.)

Allophanate of Glyceryl, $C^5H^{10}N^2O^5 = \left.\begin{matrix}C^2H^3N^2O^2\\ H^2.(C^3H^5)'''\end{matrix}\right\}O^3$. *Allophanate of Glycerin.*—Glycerin absorbs cyanic acid vapour, and is thereby converted into a white sticky mass, which dissolves in alcohol, leaving only a small quantity of cyamelide. The hot saturated solution, on cooling, deposits allophanate of glyceryl in hard crusts, composed of small translucent nodules. The crystallisation is often slow, especially when much glycerin is present; hence it is best to wash the crude product with cold alcohol before dissolving it in hot alcohol. The nodules, after recrystallisation from alcohol and drying at 100°, gave by analysis 33·6 per cent. carbon, 5·7 hydrogen, and 15·5 N, the formula requiring 33·7 C, 5·6 H, and 15·7 N.

Allophanate of glyceryl has neither taste nor smell, dissolves slowly but abundantly in water, and with tolerable facility in boiling alcohol. Heated in the dry state, it melts at about 160° C. to a colourless liquid, which solidifies in a gelatinous mass on cooling. On raising the temperature, a large quantity of carbonate of ammonium is evolved, and the mass ultimately turns brown and emits an odour of burnt horn.

It is not decomposed by *dilute acids* at ordinary temperatures, but strong nitric and sulphuric acids decompose it, with evolution of carbonic anhydride.

When triturated with water and *hydrate of barium*, it dissolves with facility; but the clear filtered solution deposits, after a short time, a bulky crystalline precipitate of carbonate of barium. The precipitation takes place even when the quantity of baryta is less than sufficient to saturate the allophanic acid present, so that it does not appear possible to prepare allophanate of barium in this manner. A certain quantity of that salt appears, however, to be formed, inasmuch as the liquid, after long standing, still deposits carbonate of barium when heated. If alcohol be added to the liquid containing an insufficient quantity of baryta, allophanate of ethyl is produced, probably by a catalytic action. Allophanate of glyceryl heated with baryta-water, yields nothing but carbonate of barium, urea, and glycerin.

In an alcoholic solution of *potash*, allophanate of glyceryl cakes together to a sticky mass, then gradually dissolves, the solution after a while depositing long needles which gradually change to small bulky masses of needles, apparently consisting of ethyl-carbonate of potassium. (Baeyer.)

Allophanate of Methyl, $C^3H^6N^2O^3 = C^2H^3(CH^3)N^2O^3$.—Discovered by Richardson in 1837 (Ann. Ch. Pharm. xxiii. 128), and originally called *ureo-carbonate of methyl*. When cyanic acid vapour is passed into methyl-alcohol, colourless crystals are obtained, which must be repeatedly washed with water, and then dried at 100° C. When heated, they partly volatilise undecomposed, and are partly resolved into ammonia, methylene gas (?), carbonic anhydride, and cyanuric acid:

$$3C^3H^6N^2O^3 = 3NH^3 + 3CH^2 + 3CO^2 + C^3H^3N^3O^3.$$

Heated with potash, they are decomposed in the same manner as the ethyl-compound. They dissolve readily in water, wood-spirit, and alcohol, especially when heated, forming neutral solutions.

Allophanate of Eugenic acid, $C^{12}H^{14}N^2O^4 = C^2H^3(C^{10}H^{11}O)N^2O^3$.—Eugenic acid rapidly absorbs cyanic acid vapour, forming a thick mass, which dissolves in hot alcohol and separates in long shining needles on cooling. At 100° C. it gave 57·0—57·9 per cent. C, 5·7—5·9 H, and 11·3 N (calc. 57·6 C, 5·6 H and 11·2 N). It contains the elements of 2 at. cyanic acid, and 1 at. eugenic acid ($2CNHO + C^{10}H^{12}O^2$), and is therefore analogous in composition to the allophanic ethers.

It is insoluble in water, sparingly soluble in cold alcohol, abundantly in hot alcohol.

It exhibits strong tendency to crystallise, so that even small quantities of the solution yield needles of proportionably considerable length. It is very soluble in ether, is destitute of taste and smell, has a silky lustre, and is permanent in the air.

Strong acids decompose it. Triturated with water and hydrate of barium, it forms a stiff paste, consisting of eugenate and allophanate of barium. Alcoholic potash does not appear to convert it into allophanate of potassium. When heated, it is resolved into eugenic and cyanuric acids. (Baeyer, Ann. Ch. Pharm. cxiv. 164.)

ALLOTROPY. See ISOMERISM.

ALLOXAN. (*Alloxanhydride*, Laurent.) $C^4H^2N^2O^4$, or $C^8H^2N^2O^8$.

History.—Discovered in 1817 by Brugnatelli, who designated it *Erythric acid:* first completely investigated by Liebig and Wöhler, in 1838 (Ann. Ch. Pharm. xxvi. 256); more recently by Schlieper (Ann. Ch. Pharm. lv. 253).

Formation and Preparation.—Alloxan is one of the numerous products of the oxidation of uric acid. Its preparation is a matter of some nicety. Liebig and Wöhler (*loc. cit.*) and Gregory (Phil. Mag. 1846), prepare it by the action of nitric acid on uric acid: concentrated nitric acid specific gravity 1·4 to 1·42), must be employed, and the temperature must not be allowed to rise above from 30° to 35° C. The process is thus conducted. From $1\frac{1}{2}$ to 2 parts strong nitric acid are placed in a beaker or porcelain basin, surrounded with cold water, and 1 pt. uric acid is added in successive small portions, with constant stirring, care being taken not to add a fresh portion of uric acid until the action caused by the addition of the former portion has quite subsided. Carbonic anhydride and nitrogen are evolved with effervescence, the action becoming gradually less violent as the operation proceeds; and crystals of alloxan gradually separate out. When the decomposition is complete, the mixture is left over night in a cool place, and the crystalline magma is then thrown on a funnel plugged with asbestos or coarsely pounded glass, and the last portions of the mother-liquor are carefully removed by washing with ice-cold water, till the washings have only a faintly acid reaction. Schlieper recommends removing the alloxan as it forms, in order to withdraw it from the further action of the nitric acid. The crystals of alloxan are dried by standing on filtering-paper or a porous tile, and then purified by solution in the smallest possible quantity of water at from 60° to 80° C.; the solution is filtered, and cooled till it crystallises: by evaporating the mother-liquor at a heat not exceeding 50° C. further crystals are obtained. The mother-liquor from these crystals, as well as that originally drained off, still contains alloxan, which is best separated by being previously converted into alloxantin. For this purpose, Schlieper proceeds as follows:—The mixed mother-liquors are *nearly* neutralised by carbonate of calcium or sodium—if the neutralisation were complete, the alloxan would be converted into alloxanic acid—and $\frac{5}{6}$ of the mixture are saturated with sulphuretted hydrogen, whereby sulphur and alloxantin are precipitated, some dialuric acid being also formed by the further action of the gas. The remaining $\frac{1}{6}$ is then added, the alloxan in which reconverts the dialuric acid formed into alloxantin. The alloxantin, which separates out completely in 24 hours, is freed from sulphur by solution in boiling water and crystallisation. In order to convert it into alloxan, one half of it is boiled with twice its volume of water, nitric acid being added drop by drop until the evolution of nitric oxide is perceptible, and the whole is heated in a water-bath until effervescence has ceased: small portions of the remaining half are then added successively, until a fresh addition produces no effervescence, then a little nitric acid, and so on till the nitric acid is completely decomposed, a little alloxantin remaining in excess. The solution is then filtered hot, and 3 or 4 drops of nitric acid added to the filtrate, which deposits crystals of alloxan on cooling. The total weight of alloxan thus obtained, should be about equal to that of uric acid employed. It is not advisable to operate on more than 70 to 80 grm. nitric acid at once.

Schlieper prefers chlorate of potassium to nitric acid as an oxidising agent. Into a basin containing 124 grm. or 4 oz. of uric acid, and 240 grm. or 8 oz. of moderately strong hydrochloric acid, he adds in successive portions, with constant stirring, 31 grm. or 6 dr. pulverised chlorate. Heat is evolved, which must not be allowed to rise above a certain limit; and a solution is obtained, containing only alloxan and urea ($C^5H^4N^4O^3 + H^2O + O = C^4H^2N^2O^4 + CH^4N^2O$). If proper care be taken, no gas is evolved. The solution is diluted with twice its volume of cold water, and decanted after three hours from any undissolved uric acid, which is heated to 50° with a little strong hydrochloric acid, and oxidised by a fresh portion of chlorate. In order to separate the alloxan from the urea, it is converted into alloxantin and reconverted into alloxan in the manner above described.

The alloxan prepared by the above methods contains 1 or 4 atoms of water of crystallisation. Anhydrous alloxan is obtained by heating the monohydrated compound to 150°—160° C. in a stream of dry hydrogen: the tetrahydrated compound must be first converted into the monohydrate by very careful heating to 100°. (Gmelin.)

Properties. — Anhydrous alloxan is of a pale reddish colour, which is probably due to the action of heat. When crystallised, it contains 1 or 4 atoms of water of crystallisation. The crystals obtained by evaporating a warm aqueous solution, contain 1 atom of water: they are oblique rhombic prisms, belonging to the monoclinic system, having the appearance of rhomboidal octahedra truncated at the extremities; they are large, transparent, and colourless, of a glassy lustre, and do not effloresce in the air. Liebig and Wöhler regarded this compound as anhydrous. Those obtained by cooling a warm saturated aqueous solution are transparent, pearly crystals, often an inch long, belonging to the trimetric system: they effloresce rapidly in warm air, and when heated to 100° are converted in the monohydrated compound. According to Gregory, there exists a third hydrate containing $2\frac{1}{2}$ atoms of water.

Alloxan is readily soluble in water or alcohol, forming colourless solutions, whence it may be precipitated by nitric acid. Its aqueous solution has an astringent taste, and colours the skin purple after a time, imparting a peculiar and disagreeable smell. It reddens litmus, but does not decompose alkaline-earthy carbonates: neither does it attack oxide of lead, even on boiling.

The following is the percentage composition of the three varieties:

C^4.	48	33·8
H^2.	2	1·41
N^2.	28	19·72
O^4.	63	45·07
$C^4H^2N^2O^4$.	142	100·00

		Calc.	Gm.
$C^4H^2N^2O^4$	142	88·75	88·65
H^2O	18	11·25	11·35
$C^4H^2N^2O^4$ + aq.	160	100·00	100·00

		Calc.	L. a. W.	Gm.
$C^4H^2N^2O^4 + H^2O$	160	74·77	73·5	74·72
$3H^2O$	54	25·23	26·5	25·28
$C^4H^2N^2O^4$ + 4 aq.	214	100·00	100·0	100·00

Decompositions. — 1. *By Heat.* When heated, alloxan melts, and is decomposed, forming, besides other products, cyanide of ammonium and urea. (Handwb. d. Chim.)

2. *By Electrolysis.* — An aqueous solution of alloxan is decomposed by the voltaic current, oxygen being evolved at the positive pole, and crystals of alloxantin formed at the negative pole.

3. *By Nitric acid.* — Hot dilute nitric acid converts alloxan into parabanic acid and carbonic anhydride:

$$C^4H^2N^2O^4 + O = \underset{\text{Parabanic ac.}}{C^3H^2N^2O^3} + CO^2$$

Further action of nitric acid converts the parabanic acid into nitrate of urea and carbonic anhydride. Monohydrated alloxan is scarcely attacked by heating with strong nitric acid. (Schlieper.)

4. *By Hydrochloric and Sulphuric acids.* — When heated with these acids, alloxan is converted into alloxantin, which gradually separates, and the mother-liquor yields on evaporation acid oxalate of ammonium. The decomposition goes through several stages: first, alloxantin, oxalic and oxaluric acids are formed; then the oxaluric acid is decomposed into oxalic acid and urea; and the urea is finally resolved into carbonic anhydride and ammonia, which last combines with the oxalic acid. (Liebig and Wöhler.)

5. An aqueous solution of alloxan is decomposed by *boiling* into carbonic anhydride, parabanic acid, and alloxantin, which separating on cooling:

$$3C^4H^2N^2O^4 = CO^2 + \underbrace{C^3H^2N^2O^3}_{\text{Parabanic acid.}} + \underset{\text{Alloxantin.}}{C^8H^4N^4O^7}$$

6. *By reducing agents*, alloxan is converted into alloxantin. This decomposition is effected by protochloride of tin, sulphuretted hydrogen, or zinc and hydrochloric acid (nascent hydrogen):

$$2C^4H^2N^2O^4 + H^2 = C^8H^4N^4O^7 + H^2O$$

the further action of the two latter reagents converts the alloxantin into dialuric acid:

$$C^8H^4N^4O^7 + H^2 + H^2O = \underbrace{2C^4H^4N^2O^4}_{\text{Dialuric acid.}}$$

The same decomposition is effected when an aqueous solution of alloxan is boiled with excess of sulphurous acid. When, however, aqueous alloxan is saturated with sulphurous anhydride, and the solution evaporated at a gentle heat, it yields on cooling large efflorescent tables of a conjugated acid, which, by analysis of its potassium-salt, appears to contain the elements of 1 atom alloxan and 1 atom sulphurous anhydride (Gregory). When a cold saturated solution of aqueous alloxan is treated with sulphurous acid in excess, ammonia added, and the whole boiled, thionurate of ammonium is formed:

$$C^4H^2N^2O^4 + NH^3 + SO^3H^2 = \underset{\text{Thionuric acid.}}{C^4H^5N^3SO^6} + H^2O$$

7. *By fixed alkalis and alkaline earths*, alloxan is converted into alloxanic acid:

$$C^4H^2N^2O^4 + H^2O = \underset{\text{Alloxanic acid.}}{C^4H^4N^2O^5}$$

Aqueous alloxan gives with baryta- or lime-water a gradual white precipitate of alloxanate of barium or calcium: a similar action is produced by a mixture of chloride of barium, or nitrate of silver, with ammonia. If the alkali be in excess, the precipitated alloxanate contains mesoxalate, and the filtrate contains urea (Schlieper). By boiling with aqueous alkalis, alloxan is decomposed into mesoxalic acid and urea:

$$C^4H^2N^2O^4 + 2H^2O = \underset{\text{Mesoxalic acid.}}{C^3H^2O^5} + \underset{\text{Urea.}}{CH^4N^2O}$$

8. *By Ammonia.*—A solution of alloxan in aqueous ammonia turns yellow when gently heated, and on cooling forms a yellow transparent jelly of mycomelate of ammonium: the liquid retains in solution alloxanate and mesoxalate of ammonium and urea (Liebig):

$$C^4H^2N^2O^4 + 2NH^3 = \underset{\text{Mycomelic acid.}}{C^4H^4N^4O^2} + 2H^2O$$

9. With *ferrous salts*, aqueous alloxan gives a deep blue colour, but no precipitate unless an alkali be added.

10. When aqueous alloxan is heated with *peroxide of lead*, carbonic anhydride is evolved, carbonate of lead precipitated, and urea is contained in the solution:

$$C^4H^2N^2O^4 + 4PbO + H^2O = CH^4N^2O + 2CO^3Pb^2 + CO^2.$$

11. When aqueous alloxan is gradually added to a boiling solution of *neutral acetate of lead*, mesoxalate of lead is precipitated, and urea remains in solution. When the lead-solution is added to the alloxan-solution, alloxantin and oxalic acid are formed.

F. T. C.

ALLOXANIC ACID. $C^4H^4N^2O^5$. = alloxan + H^2O.

History.—Discovered by Liebig and Wöhler, in 1838 (Ann. Ch. Pharm. xxvi. 292), further examined by Schlieper. (Ann. Ch. Pharm. lv. 263, lvi. 1.)

Formation and Preparation.—Alloxanic acid is formed when alloxan is brought into contact with aqueous fixed alkalis (see ALLOXAN), alkaline carbonates, or acid carbonate of calcium (Städeler). It is prepared by decomposing alloxanate of barium by sulphuric acid. The salt is suspended in a little water, and a slight excess of dilute sulphuric acid added, with constant agitation: 5 pts. salt require $1\frac{1}{3}$ pt. strong sulphuric acid, duly diluted. After digestion for some time at a gentle heat, the excess of sulphuric acid is removed by pure carbonate of lead, the excess of lead by sulphuretted hydrogen, and the excess of gas by heat: the solution is then filtered, and evaporated to a syrup, either over sulphuric acid in vacuo, or at a temperature not exceeding 40° C.

Properties.—Thus prepared, alloxanic acid forms hard white needles, arranged in radiated groups, or in warty masses: if it has been heated above 40° C. it crystallises with difficulty, or not at all. The crystals are permanent in the air: have a sour taste, but a sweetish aftertaste; are readily soluble in water, less readily, viz. in 5 to 6 pts. alcohol, still less in ether. The solution is acid to litmus, readily decomposes carbonates and acetates, and dissolves zinc, cadmium, &c., with evolution of hydrogen. Its composition is:

C^4	48	30·0
H^4	4	2·5
N^2	28	17·5
O^5	80	50·0
$C^4H^4N^2O^5$	160	100·0

It is a dibasic acid, forming acid as well as normal salts: the formula of normal alloxanates is $C^4H^2M^2N^2O^5$, of acid alloxanates, $C^4H^3MN^2O^5$. It also appears to form basic salts with some heavy metals. Alloxanates are mostly obtained by the action of aqueous alloxanic acid on metallic carbonates. The alkaline alloxanates are soluble in water: the normal salts of other metals are generally more or less insoluble, the acid salts readily soluble. They part with their water of crystallisation at temperatures varying from 100° C. to 150°; and require a stronger heat for their decomposition.

The alloxanates have been investigated principally by Schlieper (*loc. cit.*). The only one which requires special mention is the normal *barium-salt*, which is employed for the preparation of alloxanic acid. It is obtained by mixing 2 vols. of a cold saturated solution of alloxan with 3 vols. of a cold saturated solution of chloride of barium, heating the mixture to 60° or 70°, and adding gradually potash-solution, with constant agitation. Each addition of potash produces a white curdy precipitate, which soon redissolves: at last the precipitate remains permanent, and the liquid suddenly becomes filled with alloxanate of barium, which falls down as a heavy crystalline powder, and may be freed from chloride of potassium by washing with cold water. If too much potash has been added, a persistent curdy precipitate forms, consisting of basic alloxanate and mesoxalate of barium; it must be redissolved by the addition of a little alloxan-solution. A less abundant, but more certainly pure product is obtained by adding baryta-water to aqueous alloxanic acid.

Decompositions. 1. *By Heat.*—When heated, the acid melts with intumescence, becomes carbonised, and evolves vapours of cyanic acid. Alkaline alloxanates are decomposed by heat into a mixture of carbonate and cyanide. An aqueous solution of alloxanic acid is decomposed by boiling, carbonic anhydride being abundantly evolved, and two new bodies formed, one of which, *leucoturic acid*, being insoluble in water, separates as a white powder when the solution, after evaporation to a syrup, is diluted with water; while the other, *difluan*, remains in solution, but may be precipitated by alcohol. The latter is formed in far the larger quantity. The composition of these bodies is not accurately established: Schlieper assigns to the former the formula $C^3H^3N^2O^3$, to the latter, $C^3H^4N^2O^{2\frac{1}{2}}$ or $C^6H^4N^2O^5$. Schlieper states that a third substance is also formed, soluble in water and alcohol, with the formula $C^3H^5N^2O^3$. The alcoholic solution of alloxanic acid is not decomposed by boiling. Alloxanates are decomposed by boiling with water into mesoxalate and urea:

$$C^4H^4N^2O^5 + H^2O = C^3H^2O^5 + CH^4N^2O$$

2. When heated with nitric acid, alloxanic acid is decomposed into parabanic acid and carbonic anhydride:

$$C^4H^4N^2O^5 + O = C^3H^2N^2O^3 + CO^2 + H^2O.$$

3. Alloxanate of potassium gives a dark blue precipitate with ferrous-salts. (See ALLOXAN.)

Alloxanic acid is not decomposed by sulphuretted hydrogen, or by boiling with bichromate of potassium or bichloride of platinum.

According to Gmelin, the compound described by Vauquelin (Mém. du. Mus. vii. 253) by the names *acide purpurique blanc* or *urique suroxigenée* (oxuric acid) is to be regarded as impure alloxanic acid.—F. T. C.

ALLOXANTIN. (*Uroxin.*) $C^8H^4N^4O^7 + 3H^2O$ [or $C^{16}H^4N^4O^{14} + 6HO$].

History.—Probably first noticed by Prout; first described by Liebig and Wöhler in 1838; further examined by Fritzsche, who called it *uroxin* (J. pr. Chem. xiv. 237).

Formation and preparation.—Alloxantin is formed in various reactions. 1. By the action of warm dilute nitric acid on uric acid.—2. By the action of electrolysis, or of reducing agents on alloxan, or by heating it with water or dilute sulphuric acid (see ALLOXAN): also by dissolving alloxan in dialuric acid.—3. By heating dialuramide (uramil) with dilute sulphuric or hydrochloric acid, or thionurate of ammonium with a large quantity of dilute sulphuric acid.—4. By the action of the air on dialuric acid.—5. In the decomposition of caffeine by chlorine. (Rochleder.)

The following are the most usual processes for the preparation of alloxantin. 1. Dry uric acid is added gradually to warm, very dilute, nitric acid, as long as it is dissolved, and the solution evaporated till it has an onion-red colour; or dilute nitric acid is added to 1 pt. uric acid in 32 pts. water, till all is dissolved, and the solution evaporated to two-thirds; the crystals obtained in either case are purified by re-crystallisation from hot water.—2. Sulphuretted hydrogen is passed through an aqueous solution of alloxan, till a crystalline magma forms; this is dissolved by heat, the precipitated sulphur filtered off hot, and the filtrate crystallised.—3. A solution of alloxan in dilute sulphuric acid is heated for a few minutes, when it becomes turbid, and deposits crystals of alloxantin on cooling.—4. Dialurate of ammonium is evaporated at a gentle heat with a large excess of dilute sulphuric acid; when dialuric acid crystallises out, which is converted into alloxantin by the action of the air, without changing its crystalline form. (Gregory.)

Properties. — The alloxantin obtained by the above methods, contains 3 atoms of water of crystallisation, which it does not lose till heated to above 150°C. Of the properties of anhydrous alloxantin nothing is known. The crystals are small, transparent, colourless, or yellowish, oblique rhombic prisms, hard, but very friable. In those prepared by methods 1, 2, and 3, the angle of the obtuse lateral edge is 105°: in the dimorphous crystals obtained from dialurate of ammonium, it is 121°. They redden litmus, but do not exhibit acid properties in other respects. They are very slightly soluble in cold water, more abundantly, but still slowly, in boiling water, from which solution the alloxantin separates almost completely on cooling. The following is the percentage composition of anhydrous and hydrated alloxantin.

Anhydrous.		*Calc.*	*Crystals.*		*Calc.*	L. and W.	Fritzsche.
C^8	96	35·8	C^8	96	29·81	30·52	30·06
H^4	4	1·5	H^{10}	40	3·11	3·15	3·04
N^4	56	20·9	N^4	56	17·39	17·66	17·52
O^7	112	41·8	O^{10}	160	48·67	48·67	49·38
$C^8H^4N^4O^7$	268	100·0	$C^8H^4N^4O^7 + 3aq.$	322	100·00	100·00	100·00

Decompositions. — 1. *By heat*, alloxantin yields a peculiar crystalline product.

2. *By oxidising agents*, alloxantin is converted into alloxan. This change takes place slowly, when its aqueous solution is exposed to the air, much more rapidly when it is heated with chlorine-water; or when it is diffused in boiling water and a small quantity of nitric acid added. Selenious acid also converts the hot solution of alloxantin into alloxan, with separation of selenium.

3. *By reducing agents, e. g.* sulphuretted hydrogen, a hot solution of alloxantin is converted into dialuric acid:

$$C^8H^4N^4O^7 + H^2S + H^2O = \underset{\text{Dialuric acid.}}{2C^4H^4N^2O^4} + S.$$

4. When boiled with excess of hydrochloric acid, it is partly decomposed, and deposits on cooling, a white powder of alliturie acid, $C^3H^3N^2O^2$ (Schlieper). At the same time, alloxan and parabanic acid are formed, together with an acid which Schlieper calls dilituric acid, which he has not succeeded in isolating.

5. *With baryta-water*, alloxantin gives a violet precipitate, which, on boiling, turns white, and then disappears; the solution contains alloxanate and dialurate of barium,

$$C^8H^4N^4O^7 + 3BaHO = \underset{\substack{\text{Alloxanate}\\\text{Ba.}}}{C^4H^2Ba^2N^2O^5} + \underset{\text{Dialurate Ba.}}{C^4H^3BaN^2O^4} + H^2O.$$

6. *By ammonia*, alloxantin is converted into purpurate of ammonium (murexide).

$$C^8H^4N^4O^7 + 2NH^3 = \underset{\text{Murexide.}}{C^8H^8N^6O^6} + H^2O$$

This change takes place either in the wet or the dry way. In the dry way it occurs when alloxantin is heated to 100° C. in an atmosphere of dry ammonia (Gmelin): or when it is exposed at the ordinary temperature to air containing ammonia. In the wet way, an aqueous solution of alloxantin is coloured purple-red by ammonia: the colour disappears on further heating, or when left for some time in the cold. When nitric acid is gradually added to the hot alloxantin-solution, so as to form alloxan, the addition of ammonia produces a deeper purple colour as the quantity of nitric acid, and consequently of alloxan, increases; but the coloration ceases when the alloxantin is entirely converted into alloxan. When a solution of alloxantin in thoroughly boiled water is mixed with ammonia, and boiled till the purple colour has disappeared, crystals of dialuramide (uramil) are deposited: the yellow mother-liquor becomes purple by exposure to the air, deposits crystals of purpurate of ammonium, and finally coagulates into a jelly of mycomelate of ammonium:

$$C^8H^4N^4O^7 + 4NH^3 = \underset{\text{Uramil.}}{C^4H^5N^3O^3} + \underset{\substack{\text{Mycomel.}\\\text{amm.}}}{C^4H^7N^5O^2} + 2H^2O.$$

The formation of murexide depends upon the oxidation by the air of some of the uramil which is dissolved in the ammonia. When a solution of alloxantin in aqueous ammonia is repeatedly evaporated at a gentle heat in an open vessel, the residue being each time dissolved in ammonia, pure oxalurate of ammonium is finally obtained: if the air be excluded, this substance does not form.

7. Aqueous solutions of alloxantin and sal-ammoniac, both freed from air by boiling,

form a purple-red mixture, which soon becomes paler, and deposits colourless or reddish scales of uramil: the mother-liquor contains alloxan and hydrochloric acid:

$$C^8H^4N^4O^7 + NH^4Cl = \underset{\text{Uramil.}}{C^4H^5N^3O^3} + C^4H^2N^2O^4 + HCl.$$

Acetate or oxalate of ammonium acts like the chloride.

8. When aqueous alloxantin is heated with oxide of silver, carbonic anhydride is evolved, silver reduced, and oxalurate of silver formed:

$$C^8H^4N^4O^7 + 4Ag^2O + H^2O = \underset{\text{Oxalurate silver.}}{2C^3H^3AgN^2O^4} + 2CO^2 + 6Ag.$$

From nitrate of silver, alloxantin precipitates metallic silver: the filtrate gives a white precipitate with baryta-water. Aqueous alloxantin dissolves mercuric oxide with evolution of gas, probably forming mercurous alloxanate. By peroxide of lead alloxantin is converted like alloxan. — 9. Aqueous alloxantin is decomposed by long keeping, even out of contact with air, and is converted into alloxanic acid. (Gregory.)

Tetramethyl-Alloxantin, $C^8H^{14}N^4O^8 = C^4(CH^3)^4N^4O^7 + H^2O$.—This composition is assigned by Gerhardt to a product of the action of chlorine on caffeine, discovered by Rochleder (Ann. Ch. Pharm. lxxi. 1), also called *Amalic acid* (*q. v.*)—F. T. C.

ALLOYS. (See METALS.)

ALLUAUDITE. (See TRIPHYLINE.)

ALLYL. *Acryl, Propylenyl.* C^3H^5.—Berthelot and De Luca in 1854 (Ann. Ch. Phys. [3] xliii. 257), by acting on glycerin with iodine and phosphorus, obtained the compound C^3H^5I, which they regarded as *iodotritylene*, that is to say, tritylene, C^3H^6, having 1 at. H replaced by iodine, but which is now rather regarded as the iodide of the radicle allyl. Zinin, in 1855 (Ann. Ch. Pharm. xcv. 128) by acting on this iodide with sulphocyanate of potassium, obtained a volatile oil, the sulphocyanate of allyl, $C^3H^5.CyS$, identical with volatile oil of mustard, and afterwards (Ann. Ch. Pharm. xcvi. 361) prepared the benzoate, acetate, &c. of the same series. Hofmann and Cahours, in 1856 (Compt. rend. xlii. 217; more fully, Phil. Trans. 1857, 1; Ann. Ch. Pharm. cii. 285; Chem. Soc. Qu. J. x. 316), discovered allylic alcohol and prepared a great number of its derivatives. Lastly, Berthelot and De Luca in the same year isolated the radical allyl, and prepared the dibromide and diniodide. The existence of this radicle in the oils of mustard and garlic was first demonstrated by Wertheim. (Ann. Ch. Pharm. li. 289; lv. 297.)

Allyl is the third term in the series of homologous radicles C^nH^{n-1}, vinyl C^2H^3 being the second; it is the only radicle of the series that has yet been isolated.

Allyl, in the free state, $C^6H^{10} = C^3H^5.C^3H^5$, is obtained by decomposing the iodide, C^3H^5I, with sodium at a gentle heat, and afterwards distilling the liquid product. It is a very volatile liquid having a peculiar pungent, ethereal odour, somewhat like that of horse-radish. Specific gravity 0·684 at 14. Boils at 59° C. Vapour-density by experiment 2·92, by calculation from the formula C^6H^{10} (2 vol.) 2·89. Allyl is but little attacked by strong sulphuric acid. Fuming nitric acid changes it into a neutral liquid nitro-compound, soluble in ether and decomposed by heat. Chlorine acts strongly upon it, hydrochloric acid being evolved and a liquid compound formed heavier than water. Bromine and iodine unite directly with it, forming the compounds $C^3H^5Br^2$ and $C^3H^5I^2$. (Berthelot and De Luca.)

ALLYL-ALCOHOL. *Hydrate of Allyl*, $C^3H^6O = \left.\begin{matrix}C^3H^5\\H\end{matrix}\right\}O$.—Prepared by the action of ammonia on oxalate of allyl, oxamide being formed at the same time:

$$\underbrace{(C^2O^2)''(C^3H^5)^2O^2}_{\text{Oxalate of allyl.}} + 2NH^3 = 2\underbrace{(C^3H^5.H.O)}_{\text{Allyl-alcohol.}} + \underbrace{N^2.(C^2O^2)''.H^4}_{\text{Oxamide.}}.$$

Dry gaseous ammonia is passed into oxalate of allyl till the whole is converted into a solid mass of oxamide saturated with allyl-alcohol. The latter is then distilled off in a bath of chloride of calcium, and rectified over anhydrous sulphate of copper. The alcohol appears also to be produced by distilling benzoate or acetate of allyl with potash (Zinin, Ann. Ch. Pharm. xcvi. 362). It is a colourless liquid, having a pungent but not unpleasant odour, and a spirituous burning taste. It mixes in all proportions with water, common alcohol, and ether. It burns with a brighter flame than common alcohol. Boiling-point 103° C.* It gave by analysis, 62·08 per cent. C and 10·43 H, the formula C^3H^6O requiring 62·07 C, 10·34 H, and 27·59 O.

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* One sample of the alcohol very carefully prepared, was found to boil between 90° and 100° C. This, however, may have arisen from decomposition; at all events, the number 103° agrees with the differences generally observed in analogous ethyl and allyl-compounds. (Hofmann.)

Allyl-alcohol is strongly attacked by phosphoric anhydride, a colourless gas, probably C^3H^4, being given off, which burns with a very bright flame. It is violently oxidised by a mixture of acid chromate of potassium and sulphuric acid, with formation of allylic aldehyde (acrolein), C^3H^4O, and acrylic acid, $C^3H^4O^2$. The same transformation is effected, though more slowly, by platinum black. Potassium (or sodium) decomposes allyl-alcohol, with evolution of hydrogen and formation of a gelatinous mass of allylate of potassium, C^3H^4KO. Strong sulphuric acid acts on it in the same manner as on common alcohol, converting it into allyl-sulphuric acid, $C^3H^5.H.SO^4$. With potash and disulphide of carbon, it yields the potassium-salt of allyl-xanthic acid, $C^4H^6S^2O$.

ALLYL, BROMIDES OF. The *monobromide*, C^3H^5Br, which is isomeric, or perhaps identical with bromotritylene, is obtained by the action of bromide of phosphorus on allyl-alcohol (Hofmann and Cahours); or by distilling dibromide of tritylene, $C^3H^6Br^2$ (or hydrobromate of bromotritylene, $C^3H^5Br.HBr$) with alcoholic potash (Cahours). Its specific gravity is 1·47, and boiling-point 62° C. (Cahours.)

The hydrobromate of this compound, or dibromide of tritylene, is produced when bromine is gradually passed into an excess of tritylene gas; but when tritylene is passed into excess of bromine, a number of compounds are formed which may be regarded as compounds of hydrobromic acid with bromide of allyl having its hydrogen more or less replaced by bromine. (See TRITYLENE.)

Dibromide of Allyl, $C^3H^5Br^2$.—Allyl unites directly with bromine, the combination being attended with evolution of heat. If the action be stopped just as the liquid begins to show colour from excess of bromine, and to give off hydrobromic acid, and if the liquid be then treated with potash, dibromide of allyl is obtained as a crystalline body, very soluble in ether. It melts at 37° C. and when once fused, sometimes remains liquid at ordinary temperatures. It may be volatilised without decomposition (Berthelot and De Luca). The allyl in this compound takes the place of 2 at. H.

Tribromide of Allyl, $C^3H^5Br^3$.—Obtained by gradually adding bromine to iodide of allyl in a vessel surrounded by a freezing mixture. The mixture is left to itself till the next day; freed from crystallised iodine by washing first with alkaline and afterwards with pure water; then dried and distilled; the liquid which passes over is again washed and distilled, collecting apart that which goes over from 210° to 220 °C.; the purple liquid then obtained is cooled to 0° C. whereupon it solidifies in a crystalline mass; the mother-liquor is drained off; and the product is fused and again rectified. By this method, tribromide of allyl is obtained as a colourless neutral liquid, of not unpleasant odour, specific gravity 2·436 at 23° C., boiling at 217° or 218°, and solidifying below 10°. By slow solidification, it yields shining prisms, which melt at 16°. (Wurtz, Ann. Ch. Phys. [3] lx. 84.)

Alcoholic potash converts it into an ethereal substance boiling at 135° C. Heated to 100° in a sealed tube with alcoholic ammonia, it is converted into *Dibromallylamine*, $N.H.(C^3H^4Br)^2$ (M. Simpson, Phil. Mag. [4] xvi. 257). The decomposition appears to consist of two stages; in the first, the compound $C^3H^5Br^3$, is converted into $C^3H^4Br^2$, and in the second, this latter is converted into dibromallylamine:

$$C^3H^5Br^3 + NH^3 = C^3H^4Br^2 + NH^4Br.$$

$$\text{and}\qquad 2C^3H^4Br^2 + 3NH^3 = N\begin{cases} C^3H^4Br \\ C^3H^4Br \\ H \end{cases} + 2NH^4Br.$$

Dissolved in glacial acetic acid, and heated with acetate of silver to 120°—125° C. for a week, it yields bromide of silver and triacetin (p. 25.)

$$C^3H^5.Br^3 + O^3\begin{cases}(C^2H^3O)^3 \\ Ag^3\end{cases} = O^3\begin{cases}(C^3H^5)''' \\ (C^2H^3O)^3\end{cases} + 3AgBr.$$

The radicle C^3H^5 in this compound is triatomic, replacing 3 at. hydrogen, as seen in the reaction just mentioned; in other words the compound is formed on the type $H^3.H^3$. Wurtz has obtained two compounds (or perhaps only one) isomeric with it, by the action of bromine on bromotritylene, C^3H^5Br, and on the isomeric body bromide of allyl. These compounds are perhaps formed on the type $H^2.H^2$, their rational formula being $C^3H^4Br.Br^2$. They both have a specific gravity of 2·392 at 23° C., and boil at about 195°; but they differ somewhat in odour and in their action on silver-salts, the former being more energetic in both respects than the latter (Wurtz). The action of bromide of bromallyl on ammonia is totally different from that of tribromide of allyl, giving rise, not to dibromallylamine, but to the compound $C^3H^4Br^2.C^3H^5Br^4$. (Simpson.)

ALLYL, CHLORIDE OF. *Chlorotritylene*, C^3H^5Cl, is obtained like the bromide, by the action of chloride of phosphorus on allyl-alcohol, or by treating chloride of tritylene, $C^3H^6.Cl^2$ (hydrochlorate of allyl-chloride, $C^3H^5Cl.HCl$) with alcoholic potash. The last mentioned compound treated with excess of chlorine yields substitution-products similar to those obtained with the bromide. (See TRITYLENE.)

ALLYL HYDRIDE OF, $C^3H^6 = C^3H^5.H$.—Tritylene or propylene, the third term in the series of hydrocarbons C^nH^{2n}, is perhaps the hydride of allyl.

ALLYL, IODIDES OF. The *monoiodide* (iodotritylene) C^3H^5I, is obtained by distilling glycerin at a gentle heat with diniodide of phosphorus;

$$2C^3H^8O^3 + 2PI^2 = 2C^3H^5I + P^2O^3 + 3H^2O + 2I.$$

A quantity of tritylene-gas is given off, due to a secondary action, and a mixture of oxygen-acids of phosphorus with iodine and undecomposed glycerin remains in the retort. Tri-iodide of phosphorus may also be used, but the action is less regular. The distillate is purified by rectification, the portion which passes over at 100° C. being collected apart (Berthelot and De Luca). Iodide of allyl is also produced by the action of iodine and phosphorus on allyl-alcohol. (Hofmann and Cahours.)

When first prepared, it is colourless, and has an ethereal alliaceous odour; but by the action of air and light, it becomes coloured and then gives off irritating vapours Specific gravity 1·789 at 160° C. Boiling-point 101°. It is insoluble in water, but dissolves in alcohol and ether. By the action of zinc or mercury, and hydrochloric or dilute sulphuric acid, it is converted into tritylene (hydride of allyl):

$$C^3H^5I + 4Hg + HCl = C^3H^6 + Hg^2Cl + Hg^2I.$$
$$\text{and} \quad C^3H^5I + 2Zn + HCl = C^3H^6 + ZnCl + ZnI.$$

Iodide of allyl is decomposed by silver-salts, iodide of silver being formed, and the acid radicle being transferred to the allyl.

Diniodide of Allyl, $C^3H^5I^3$.—Obtained by dissolving 6 or 7 pts. of iodine in 1 pt. of allyl at a gentle heat. The mixture, which is liquid at first, solidifies after a few minutes; and by triturating the mass with aqueous potash, then digesting in boiling ether, and evaporating the ethereal solution, the diniodide of allyl is obtained in the crystalline form. It is decomposed by distillation, yielding iodine and a neutral liquid. It is scarcely attacked by aqueous potash; but alcoholic potash decomposes it, producing a liquid which smells like allyl. It is not acted upon by mercury and hydrochloric acid. (Berthelot and De Luca.)

Iodide of Mercurallyl, $C\,H^5Hg^2I$, is obtained by agitating iodide of allyl with metallic mercury. On crystallising the resulting yellow mass from a boiling mixture of alcohol and ether, nacreous scales are formed, which turn yellow when exposed to light, especially if moist. They dissolve but sparingly in cold alcohol, and are nearly insoluble in boiling alcohol. Heated to 100° C. they sublime in rhombic plates; at 135° they melt, and solidify in a crystalline mass on cooling. When quickly heated, they decompose, yielding a yellow sublimate and a carbonaceous residue. The alcoholic solution treated with oxide of silver, yields a strongly alkaline liquid, which when evaporated leaves a syrupy mass, probably consisting of hydrate of mercurallyl. (Zinin.)

ALLYL, OXIDE OF. *Allylic ether*, $(C^3H^5)^2O$, is produced by the action of iodide of allyl on allylate of potassium:

$$C^3H^5KO + C^3H^5I = KI + (C^3H^5)^2O;$$

also by the action of oxide of silver or oxide of mercury on iodide of allyl:

$$2C^3H^5I + Ag^2O = 2AgI + (C^3H^5)^2O.$$

A body having the same composition was obtained by Wertheim (Ann. Ch. Pharm. li. 309; lv. 297), by acting on oil of garlic, $(C^3H^5)^2S$, with nitrate of silver, and distilling the crystalline product thereby produced; also by heating oil of mustard (sulphocyanate of allyl), with fixed alkalis, *e. g.* with soda-lime.

Oxide of allyl is a colourless liquid, lighter than water, and insoluble in water. It boils at 82° C. (Hofmann and Cahours); between 85° and 87° C. (Berthelot and De Luca). It forms with sulphuric acid a conjugated acid yielding a soluble barium-salt. Nitric acid converts it into a nitro-compound heavier than water. With iodide of phosphorus, it yields iodide of allyl. Heated with butyric acid it is decomposed, with formation of butyrate of allyl. (B. and L.)

Ethyl-allyl-ether, $C^5H^{10}O = C^2H^5.C^3H^5.O$, is obtained by the action of iodide of ethyl on allylate of potassium, or of iodide of allyl on ethylate of potassium. It is a colourless aromatic, very volatile liquid, boiling at about 84° C. Similar compounds are produced by treating iodide of allyl with methylate, amylate, and phenylate of potassium (Hofmann and Cahours). *Amyl-allyl-ether* boils at about 120° C. (Berthollet and De Luca.)

Oxide of Allyl and Glyceryl, or Triallylin, $C^{12}H^{20}O^{6} = \left.\begin{matrix}(C^3H^5)'''\\(C^3H^5)^3\end{matrix}\right\} O^6$.—Iodide of allyl distilled with potash and glycerin yields this compound in the form of a liquid, boiling at 232° C., soluble in ether, and having a disagreeable odour. (Berthelot and De Luca):

$$(C^3H^5)'''.H^3.O^3 + 3C^3H^5I = 3HI + (C^3H^5)'''.(C^3H^5)^3O^3.$$

The formula is that of a triple molecule of water H^6O^3, in which 3 at. H are replaced by the triatomic radicle glyceryl, and the other three by 3 at. of the monatomic radicle allyl.

ALLYL, OXYGEN-SALTS OF. Acetate, oxalate, sulphate, &c. (See the several acids.)

ALLYL, SULPHIDE OF. *Oil of garlic*, $C^6H^{10}S = (C^3H^5)^2S$ [or C^6H^5S].—This compound is produced by distilling iodide of allyl with protosulphide of potassium:

$$2C^3H^5I + K^2S = 2KI + (C^3H^5)^2S,$$

and is contained in the essential oils produced by distilling with water the leaves and seeds of various plants of the liliaceous and cruciferous orders. It forms the principal constituent of the oil obtained from the bulbs of garlic (*Allium sativum*), from which it was first obtained in the pure state by Wertheim in 1844; and it exists in smaller quantity in oil of onions (*Allium cepa*). It occurs also, together with 10 per cent. of oil of mustard (sulphocyanate of allyl), in the herb and seeds of *Thlaspi arvense*, passing over when these matters are bruised with water and distilled. The leaves of *Alliaria officinalis* distilled with water yield oil of garlic; the seeds yield oil of mustard (Wertheim). The bruised seed distilled after maceration in water, yields a mixture of 10 per cent. oil of garlic, and 90 oil of mustard; but the seed produced in sunny places yields only the latter. The herb and seeds of *Thlaspi arvense* yield a mixture of 90 per cent. oil of garlic, and 10 oil of mustard. The herb and seeds of *Iberis amara* likewise yield a mixture of the two oils; and very small quantities of the same mixture are obtained from the seeds of *Capsella Bursa Pastoris*, *Raphanus Raphanistrum*, and *Sisymbrium Nasturtium*. (Pless, Ann. Ch. Pharm. lviii 36.)

To obtain the whole of the mixed oils, the several parts of the plants, especially the seeds, must be macerated in water some time before distillation. For, in the seeds of *Thlaspi arvense*, for example, the oils do not exist ready formed; the seeds, in fact, emit no odour when bruised, and if before distillation with water, they are heated to 100° C. or treated with alcohol, no oil passes over; and if the seed be exhausted with alcohol, and the filtrate evaporated, there remains a crystalline residue mixed with mucus, which, when triturated with water and with the seed of *Sinapis arvensis*, yields, not oil of garlic, but oil of mustard. (Pless, Ann. Ch. Pharm, lviii. 36.)

Preparation. a. From Iodide of Allyl.—The iodide is cautiously dropped into a concentrated alcoholic solution of sulphide of potassium, the liquid then becoming very hot, and an abundant crystalline deposit of iodide of potassium being formed. As soon as the action ceases, the liquid is mixed with a slight excess of sulphide of potassium; water is then added, and the oil which rises to the surface is rectified.

b. From Garlic.—The crude oil is obtained by distilling bruised garlic-bulbs with water in a large still. The oil passes over with the first portions of water, the product amounting to 3 or 4 oz. from 100 pounds of the bulbs. The milky water which passes over at the same time, contains a large quantity of oil in solution, and serves therefore for cohobation. The crude oil is heavier than water, of dark brownish-yellow colour, and has a most intense odour of garlic. It decomposes at 140° C.; that is to say, somewhat below its boiling-point, which is 150°, becoming suddenly heated, assuming a darker colour, and giving off intolerably stinking vapours, without yielding a trace of garlic oil; the residue is a black-brown glutinous mass. (Wertheim.)

Preparation of the rectified oil.—The crude oil is distilled in a salt-bath (in the water-bath the distillation is slower) as long as anything passes over. One-third of the crude oil remains behind as a thick dark-brown residue. The rectified oil is lighter than water, and of a pale yellow colour, or after two distillations, colourless, and smells like the crude oil, though less offensive. Does not evolve a trace of of ammonia when treated with hydrate of potash. It covers potassium with a liver-coloured film of sulphide of potassium, depositing an organic substance, and giving off a small quantity of a gas which burns with a pale blue flame. With fuming nitric acid, oil of vitriol, hydrochloric acid gas, dilute acids and alkalis, corrosive sublimate, nitrate of silver, bichloride of platinum and nitrate of palladium, it behaves like pure sulphide of allyl. Even after being several times rectified and dried with chloride of calcium, it exhibits a variable composition and a certain amount of oxygen, and must therefore contain, besides sulphide of allyl, an oxygen compound, probably oxide of allyl, the presence of which is indeed indicated by the reaction with potassium. (Wertheim.)

Preparation of pure Oil of Garlic or *Sulphide of Allyl.*—The rectified oil is again rectified several times; dehydrated over chloride of calcium; decanted; a few pieces of potassium introduced into it; and as soon as the evolution of gas thereby produced has ceased, the oil is quickly distilled off from the residue. The rectified oil appears to contain oxide as well as sulphide of allyl, together with excess of sulphur, these impurities either pre-existing in the crude oil, or being formed from sulphide of allyl by the action of atmospheric oxygen, that portion of the sulphide which takes up the oxygen, giving up its sulphur to the rest. If the potassium be not suffered to complete its action before the liquid is distilled, it merely removes the excess of sulphur, but does not decompose the oxide of allyl, and a distillate is obtained, containing from 65·17 to 64·75 per cent. C, and 9·22 to 9·15 H. (Wertheim.)

Properties.—Colourless oil, of great refracting power, and lighter than water. Boils at 140° C. May be distilled without decomposition. Smells like the crude oil but less disagreeably. It dissolves sparingly in water, readily in alcohol and ether.

	Calculation.		Wertheim.
6C	72	63·16	63·22
10H	10	8·77	8·86
S	32	28·07	27·23
$(C^3H^5)^2S$	114	100·00	99·31

Decompositions.—1. Sulphide of allyl dissolves with violent action in *fuming nitric acid;* the solution when diluted with water, deposits yellowish-white flakes, and is found to contain oxalic and sulphuric acids; according to Hlasiwetz (J pr. Chem. li. 355) oil of garlic treated with nitric acid, yields formic and oxalic acids.—2. With cold *oil of vitriol*, it forms a purple solution, from which it is separated by water, apparently without alteration.—3. It absorbs *hydrochloric acid gas* in large quantities; the deep indigo-coloured mixture becomes gradually decolorised on exposure to the air, and immediately if gently heated or diluted with water.—4. From *nitrate of silver*, it throws down a large quantity of sulphide of silver, whilst nitrate of silver and allyl remains in solution (Wertheim). It is not altered by dilute acids or alkalis, or by potassium.

Combinations.—Sulphide of allyl does not precipitate the aqueous or alcoholic solutions of acetate of nitrate of lead, or acetate of copper; neither does it precipitate the solution of arsenious or arsenic acid in aqueous sulphide of ammonium.

With solutions of *gold, mercury, palladium, platinum,* and *silver,* it forms precipitates, consisting of a double sulphide of allyl and the metal, either alone or associated with a double chloride.

Gold-precipitate.—Sulphide of allyl forms with aqueous trichloride of gold, a beautiful yellow precipitate, which resembles the platinum-precipitate, but soon cakes together in resinous masses, and becomes covered with films of gold.

Mercury-precipitate.—Alcoholic solutions of oil of garlic and corrosive sublimate form a copious white precipitate, which when left to stand for some time, and especially if diluted with water, increases to a still greater quantity. It is a mixture of the compounds *a* and *b*, which may be separated by continued boiling with strong alcohol, only the compound *a* being soluble therein. (Wertheim.)

a. The alcoholic filtrate, when left to itself or evaporated with water, and after washing and drying, yields a white powder, agreeing in composition with the formula $(C^3H^5)^2S.2Hg^2S + 2(C^3H^5Cl.2HgCl)$, or $2(C^3H^5)^2S.Hg^2S.6HgCl$ (anal. 10·91 C, 1·61 H, 63·67 Hg, and 16·41 Cl:—calc. 11·32 C, 1·57 H, 62·87 Hg, and 16·70 Cl). It blackens superficially on exposure to the sun; when heated, it gives off vapours smelling like onions, and yields a sublimate of calomel and mercury. When immersed in moderately strong potash-ley, it acquires a light yellow colour from separation of oxide of mercury; if this oxide be then removed by dilute nitric acid, there remains a white substance, probably = $(C^3H^5)^2S.2Hg^2S$. When distilled with sulphocyanate of potassium, it yields oil of mustard, together with other products. It is insoluble in water, and dissolves but sparingly in alcohol and ether. (Wertheim.)

b. The portion of the mercury-precipitate insoluble in hot alcohol contains the same constituents, and has the carbon and hydrogen likewise in the ratio of 6 : 5 at., but is much richer in mercury. (Wertheim.)

Palladium-precipitate.—When rectified oil of garlic is gradually added to a solution of nitrate of palladium, kept in excess, a brown precipitate is formed, which appears to contain $2C^6H^{10}S.3Pd^2S$.—Chloride of palladium forms with oil of garlic a yellow precipitate, probably consisting of the preceding compound mixed with chloride of palladium.

Platinum-precipitate.—Oil of garlic forms a yellow precipitate with dichloride of platinum. This precipitate is obtained of a finer yellow colour by the use of alcoholic solutions; but when strong alcohol is used, its formation is gradual, becoming instantaneous however on addition of water. If the water be added too quickly and in too great quantity, the precipitate is yellowish-brown, resinous, and difficult to purify; the addition of water must therefore be stopped as soon as a strong turbidity appears; in that case, if the oil of garlic is not in excess, a copious flocculent precipitate is sure to be obtained, resembling chloro-platinate of ammonium. The precipitate is washed on the filter, first with alcohol, then with water, and dried at 100° C.—When heated considerably above 100°, it changes colour, and leaves sulphide of platinum in so porous a condition that it takes fire at a higher temperature, and continues to glow till it is reduced to pure platinum. Fuming nitric acid decomposes and dissolves the precipitate completely, forming dichloride of platinum and platinic sulphate. When immersed in hydrosulphate of ammonium, it is gradually converted into the kermes-brown compound next to be described. Aqueous potash and sulphuretted hydrogen have no action upon it. The precipitate is nearly insoluble in water, and dissolves but sparingly in alcohol and ether. It gives by analysis 17·85 per cent. C, 2·87 H, 48·53 Pt, 18·29 S, and 13·22 Cl, whence Wertheim deduces the somewhat improbable formula, $3(C^6H^{10}S.2PtS) + 2(C^3H^5Cl.PtCl^2)$, which requires 17·77 C, 2·47 H, 48·88 Pt, 17·77 S, and 13·11 Cl.

Kermes-brown compound, $(C^3H^5)^2S.2PtS$.—Formed, together with dissolved sal-ammoniac, when the platinum-precipitate just described is left in contact and shaken up with hydrosulphate of ammonium. The brown compound heated to 100° C. emits an alliaceous odour, and gives off 4·88 per cent. of sulphide of allyl. The darker substance containing excess of platinum which remains, continues unaltered till it is heated to 140° C. but between 150° and 160°, gives off 5·17 per cent. more, therefore in all 9·55 per cent. of sulphide of allyl, leaving a still darker compound of $(C^3H^5)^2S$ with 3PtS. The kermes-brown compound is insoluble in water, alcohol, and ether. (Wertheim.)

Silver-precipitate.—When a solution of nitrate of silver in aqueous ammonia is mixed with excess of sulphide of allyl, one portion of the compound resolves itself into oxide of allyl, which rises to the surface as an oil, and nitrate of ammonium; but there is also formed at the beginning a white or pale yellow precipitate, which perhaps consists of $(C^3H^5)^2S + xAg^2S$. For if it be immediately washed with alcohol, and dried between paper, it is resolved by distillation into sulphide of allyl and a residue of sulphide of silver. But if it remains half an hour immersed in the liquid, it assumes a continually darker brown colour, and is finally converted into black sulphide of silver. (Wertheim.)

ALLYL and HYDROGEN, SULPHIDE OF. *Allyl-mercaptan*, $C^3H^6S = C^3H^5.H.S$.—Produced by distilling iodide of allyl with sulphide of hydrogen and potassium:

$$C^3H^5I + KHS = KI + C^3H^5.H.S.$$

It is a volatile oily liquid, having an odour like that of oil of garlic, but more ethereal. It boils at 90 °C. It is powerfully attacked by nitric acid, assuming a red colour, and yielding an acid analogous to ethyl-sulphurous acid. It acts with great energy on mercuric oxide, forming a compound C^3H^5HgS, which dissolves in boiling alcohol, and separates from the solution in pearly scales resembling mercaptide of mercury. (Hofmann and Cahours.)

ALLYL, SULPHOCYANATE OF. $C^4H^5NS = CNS.C^3H^5$.—*Volatile oil of Mustard.* (See SULPHOCYANIC ETHERS.)

ALLYL-SULPHOCARBAMIC, or SULPHOSINAPIC ACID. $C^4H^7NS^2 = S \left\{ \begin{matrix} N.(CS)''.C^3H^5.H \\ H \end{matrix} \right.$.—This acid is not known in the separate state, but its soluble salts, viz. those containing the metals of the alkalis and alkaline earths, are obtained by treating oil of mustard with the hydrosulphates of those metals: *e. g.*

$$C^4H^5NS + KHS = C^4H^6KNS^2.$$

It may be regarded either as composed according to the preceding formula, that is to say, as hydrosulphate of ammonium, $NH^4.H.S$, having 1 at. H in the ammonium-molecule replaced by allyl and two more by the diatomic radicle CS, or as a compound of sulphocyanide of allyl with sulphide of hydrogen. The mode of formation leads directly to the latter view. (See SULPHOSINAPIC ACID.)

ALLY-SULPHOCARBONIC, or **ALLYL-XANTHIC ACID.** *Sulphide of Allyl, Carbonyl, and Hydrogen,* $C^4H^6S^2O = S^2\left\{\begin{matrix}(CO)''\\ H.C^3H^5\end{matrix}\right.$—When allyl-alcohol is treated with potash and disulphide of carbon, a salt is formed, which crystallises in yellow needles like xanthate of potassium. (Hofmann and Cahours.)

ALLYL-SULPHURIC ACID. $C^3H^5.H.SO^4$.—*Sulphate of Allyl and Hydrogen.* (See SULPHURIC ETHERS.)

ALLYL-UREA. (See CARBAMIDE.)

ALLYLAMINE. $C^3H^7N = N.H^2.(C^3H^5)$, is obtained by the action of ammonia on iodide of allyl, or by boiling cyanate of allyl with strong aqueous potash

$$CNO.C^3H^5 + 2KHO = CO^3K^2 + N.H^2(C^3H^5).$$

If the alkaline distillate be condensed in hydrochloric acid, a saline mass is obtained, which when distilled with potash, yields, among other products, a basic oil having the composition of allylamine. The platinum-salt, $C^3H^7N.HCl.PtCl^2$, separated from solution by slow evaporation forms magnificent crystals.

DIALLYLAMINE, $C^6H^{11}N = N.H.(C^3H^5)^2$, is formed, together with other products, by the action of iodide of allyl on allylamine.

DIBROMALLYLAMINE, $C^6H^9Br^2N = N.H.(C^3H^4Br)^2$.—Produced by the action of ammonia on tribromide of allyl (p. 141).

$$2C^3H^5Br^3 + 5NH^3 = C^6H^9Br^2N + 4NH^4Br.$$

1 vol. tribromide of allyl is mixed with about 6 vol. of a solution of ammonia in weak alcohol, and heated to 100° C. in sealed tubes for 10 or 12 hours; the liquid is then filtered from the separated bromide of ammonium, and the filtrate mixed with a large quantity of water, whereupon it becomes turbid, and deposits dibromallylamine in the form of a heavy oil, which may be purified by dissolving it in hydrochloric acid, evaporating to dryness at 100° C., redissolving in water, filtering to separate a small quantity of oil, again evaporating, and treating the residue with ether, in which the hydrochlorate is nearly insoluble. From the salt thus purified, the base is separated by distillation with potash. It is alkaline to test-paper, and forms a cloud with hydrochloric acid: it is however but a weak base, incapable of decomposing the salts of copper or silver. It cannot be distilled without alteration. It is but sparingly soluble in water, but dissolves readily in alcohol and in acids. It has a peculiar sweet and aromatic taste. It does not show much tendency to form crystallisable salts. The *sulphate* forms a gummy mass.—The hydrochlorate is a yellowish salt easily soluble in water and alcohol, sparingly in ether. It tastes like the base itself. It assumes a darker colour at 100° C. and sublimes partially at 160°. On adding nitrate of silver to the aqueous solution, the whole of the chlorine is precipitated as chloride of silver, but the bromine remains in solution. The *chloroplatinate*, $C^6H^9Br^2N.HCl.PtCl^2$, is an orange-coloured precipitate nearly insoluble in absolute alcohol. Alcoholic solutions of dibromallylamine and chloride of mercury form, when mixed, a copious white precipitate. (Maxwell Simpson, Phil. Mag. [4] xvi. 257.)

Ethyldibromallylamine, $C^8H^{13}Br^2N = N.C^2H^5.(C^3H^4Br)^2$. — Obtained by enclosing dibromallylamine with a large excess of iodide of ethyl in a sealed tube, and heating the mixture to 100° C. for a considerable time. The excess of iodide of ethyl is then distilled off, and the remaining hydriodate of ethylbibromallylamine is dissolved in water and distilled with potash. It has a very bitter and pungent taste, smells like nutmeg, is insoluble in water, soluble in acids, and alkaline to test-paper. It is a stronger base than dibromallylamine, and precipitates oxide of copper from cupric salts. (Simpson.)

TRIALLYLAMINE, $C^9H^{15}N = N.(C^3H^5)^3$, is formed by the destructive distillation of hydrate of tetrallylium.

TETRALLYLIUM, $C^{12}H^{20}N = N(C^3H^5)^4$.—The iodide of this base is the chief product of the action of ammonia on iodide of allyl. The action takes place without the aid of heat, a large quantity of the iodide dissolving after a few days' contact; the solution afterwards deposits splendid crystals of the iodide, and sometimes becomes a solid mass. The separation of the crystals may be accelerated by adding a strong solution of potash, in which the iodide is completely insoluble. The iodide is purified by exposing it to the air till the potash is converted into carbonate, and then recrystallising from absolute alcohol. Treated with oxide of silver, it yields the hydrated oxide of tetrallylium, and the solution of this oxide mixed with hydrochloric acid and bichloride of platinum, forms a yellow salt containing $N(C^3H^5)^4Cl,PtCl^2$.

Tetrallylarsonium, $As(C^3H^5)^4$.—When iodide of allyl is digested with arsenide of potassium, several liquid compounds are formed, having a very fetid odour, and at the same time a solid crystalline body separates, which is the iodide of tetrallyl-arsonium. (Hofmann and Cahours.)

ALLYLENE. C^3H^4.—A diatomic radicle which bears to allyl the same relation that ethylene C^2H^4, bears to ethyl C^2H^5. Respecting its properties in the free state and the mode of separating it, see ADDENDA (p. 1112).

Chloride of Allylene, $C^3H^4.Cl^2$. *Acroleinchlorid.*—Obtained by the action of perchloride of phosphorus on acrolein (p. 56). To prevent the action from becoming too violent, the retort should be externally cooled, the perchloride of phosphorus covered with a layer of oxychloride, and the acrolein added by small portions at a time. The proportions are 1 pt. acrolein to 3 pts. of the perchloride. The crude distillate is shaken up with water to remove oxychloride of phosphorus, and further purified by digestion with chloride of calcium and rectification, the chloride of acrolein passing over at about 90° C. It is a colourless oil, having a sweetish ethereal taste, and an odour like that of chloroform. Specific gravity 1·170 at 27·5 C. Boiling-point (corrected) 84·4° C.—Another oily liquid, apparently isomeric with chloride of allylene, is likewise formed by the action of perchloride of phosphorus on acrolein.

Chloride of allylene is slowly oxidised by nitric acid. Heated with aqueous nitrate of silver, it precipitates chloride of silver. Chlorine converts it into a crystalline compound, probably sesquichloride of carbon. Sodium has no action upon it. Heated with ethylate of sodium, it appears to yield a compound corresponding to acetal (p. 3). Heated in a sealed tube with alcoholic potash, it appears to yield the same compound, together with *chloride of acryl*, C^3H^3Cl. Heated in a sealed tube with ammonia, it yields sal-ammoniac and acrolein-ammonia (p. 56). (Hübner and Geuther, Ann. Ch. Pharm. cxiv. 36.)

Acetate of Allylene, $C^7H^{10}O^4 = \left.\begin{matrix}(C^3H^4)''\\(C^2H^3O)^2\end{matrix}\right\}O^2$. *Acetate of Acrolein.*—Produced, 1. By heating in sealed tubes a mixture of 1 at. acrolein (C^3H^4O), and 1 at. acetic anhydride ($C^4H^6O^3$.)—2. By heating 1 at. chloride of allylene with 2 at. acetate of silver in a sealed tube, first in the water-bath for several hours, then to 160° C. in an oil-bath, rectifying the product, and collecting apart that which passes over between 135° and 160°: $C^3H^4Cl^2 + (C^2H^3O)^2.Ag^2.O^2 = (C^2H^3O)^2.C^3H^4.O^2 + 2AgCl$. It is a colourless liquid, having a strong fishy odour, and very sharp taste. Specific gravity 1·076 at 22° C.; boils at about 180°. It slowly reduces an ammoniacal solution of nitrate of silver. Heated with caustic-potash, it yields acrolein and acetate of potassium. It may he regarded as a compound of 1 at. acrolein with 1 at. acetic anhydride, $C^3H^4O.C^4H^6O^3$. (Hübner and Geuther.)

ALMAGRERITE. Native anhydrous sulphate of zinc. (See SULPHATES.)

ALMANDINE. (See GARNET.)

ALMONDS, OIL OF.—Both sweet and bitter almonds yield by pressure a fixed oil, having a light yellow colour, an agreeable taste, but no odour. Specific gravity 0·918 at 15°. It consists chiefly of olein, with but little solid fats, and consequently requires a very low temperature (−25° C.) to solidify it. It easily turns rancid. It dissolves in 25 pts. of cold alcohol, in 6 pts. of boiling alcohol, and mixes in all proportions with ether.

Bitter almonds macerated with cold water and distilled, yield also a volatile oil, of fragrant odour, which is the *hydride of benzoyl* ($C^7H^5O.H$). This oil does not exist ready formed in the almonds, but is produced by the action of an azotised body, *emulsin*, on the amygdalin contained in the fruit. Sweet almonds do not contain emulsin, and therefore do not yield the volatile oil. (See BENZOYL, HYDRIDE OF.)

ALOERETIC ACID. (See ALOETIC ACID.)

ALOES. The thickened juice of various species of aloe, a genus of plants belonging to the liliaceous order. It is chiefly extracted from the *Aloe soccotrina* in Arabia; from *Aloe spicata* and *A. linguiformis* at the Cape of Good Hope; and from *A. vulgaris* or *sinuata* in Barbadoes and Jamaica. The best sorts of aloes are prepared by exposing to the sun the juice which exudes spontaneously from incisions in the leaves; inferior kinds are obtained by pressing the leaves. Aloes occurs in commerce in large red-brown masses, having a shining conchoidal fracture; in thin plates it is red and translucent; it is easily reduced to a yellow powder. It has an odour like that of saffron, and a very persistent bitter taste. It dissolves completely in alcohol and in boiling water. It possesses active purgative properties, due to a crystallisable principle *aloin*, which is contained in it, and may be extracted in a state of purity from Barbadoes aloes.

ALOETIC ACID. $C^{14}H^{4}N^{2}O^{12}$? *Polychromic Acid. Artificial Bitter of Aloes.*—Produced by the action of nitric acid upon aloes, chrysammic acid being formed at the same time (Schunck, Ann. Ch. Pharm. xxxix. 24; lxv. 235; G. J. Mulder, J. pr. Chem. xlviii. 39). 1 part of aloes is gently heated with 8 pts. of moderately strong nitric acid till gas begins to escape; the vessel is then removed from the fire, and as soon as the disengagement of gas ceases, the solution is concentrated by evaporation, till a yellow powder separates, the quantity of which may be increased by addition of water. The aloetic acid is separated from the chrysammic acid in this powder by treatment with boiling alcohol, which dissolves the aloetic acid; and on evaporating the solution, the acid is obtained in the form of an orange-yellow powder having a bitter taste. It is but slightly soluble in water, but dissolves more freely in boiling water, forming a solution of a splendid purple colour, which is changed to yellow by nitric acid, but restored by alkalies. It is dissolved by ammonia, potash, and soda, forming purple solutions. Strong nitric acid converts it into chrysammic acid. It is monobasic. The *barium*-salt, $C^{7}H^{3}BaN^{2}O^{6}$, is a brown-red nearly insoluble powder, obtained by precipitating the aqueous acid with acetate of barium. The *potassium*-salt separates by slow evaporation in crystals of a fine ruby colour. According to Schunck, the formula of aloetic acid is $C^{16}H^{4}NO^{13}$; according to Mulder $C^{14}H^{3}N^{2}O^{11}$. According to the formula above given, it is isomeric with dinitrobenzoic acid.

The alcoholic mother-liquor obtained in the preparation above described contains another acid called *Aloeretic acid*, $C^{7}H^{3}ON^{6}$? which, according to Mulder, is the first product of the action of nitric acid on aloes. It is separated by neutralising with chalk, mixing the filtrate with acetate of lead, decomposing the lead-precipitate with hydrosulphuric acid, and evaporating. It is a brown amorphous mass, which when boiled with nitric acid is converted first into aloetic, then into chrysammic acid. (Mulder.)

The name aloeretic acid is also applied by Schunck to an acid produced by the action of alkalis on chrysammic acid, and called by Mulder *chrysatric acid* (which see).

ALOÏN. $C^{17}H^{18}O^{7}$, or $C^{34}H^{18}O^{14}$.—A crystalline bitter principle obtained from aloes: also called *Bitter of aloes.* It is prepared by mixing Barbadoes aloes with sand, to prevent agglomeration, treating it several times with cold water, and evaporating the aqueous extract in vacuo to the consistence of a syrup. It then separates in small crystals. The solution must not be heated to the boiling-point, since aloïn undergoes alteration at 100° C.

According to Dr. Stenhouse (Phil. Mag. [3] xxxvii. 481), the Cape and Socotrin aloes contain large quantities of foreign matters which prevent the crystallisation of the aloïn; he has succeeded in isolating the aloïn, only by operating on the Barbadoes aloes.

Pure aloïn separates from an alcoholic solution, in the form of small prismatic needles, grouped in stars, of a pale yellow colour. Its taste is at first sweet, then extremely bitter. It is much more purgative than aloes itself. In the cold, it is but slightly soluble in water and alcohol, but dissolves better when hot; the solutions are yellow and neutral to test-paper. Dried at 100°C. it contains $C^{17}H^{18}O^{7}$.

The caustic and carbonated *alkalis* dissolve aloïn with a bright yellow colour.

By digestion with concentrated *nitric acid*, aloïn is transformed into chrysammic acid. *Chlorine* passed into an aqueous solution of aloïn, produces a bright yellow precipitate, *chloraloïl*, containing, according to Robiquet, $C^{13}ClO^{5}$. Solution of *chloride of lime* colours aloïn bright yellow, this tint passing rapidly to brown.

Bromine added in excess to a cold aqueous solution of aloïn produces a yellow precipitate of *bromaloïn*, $C^{17}H^{15}Br^{3}O^{7}$? which dissolves in boiling alcohol, and separates in shining yellow needles, grouped in stars, and much larger than the crystals of aloïn. It is less soluble in cold water and alcohol than aloïn: the solutions are neutral.

ALOISOL.—$C^{6}H^{8}O^{2}$? An oily liquid obtained in very small quantity by distilling aloes with half its weight of quick lime. It is colourless, has a sharp penetrating odour, is insoluble in water, but mixes in all proportions with alcohol and ether. Specific gravity 0·877. Boiling-point 130°C. By contact with the air, or by the action of strong nitric acid on chlorine water, it is converted into a brown-red liquid, heavier than water, and having a very decided odour of castoreum. Treated with oxide of copper or chromic acid, it yields carbonic acid, water, and hydride of benzoyl. (Robiquet, J. Pharm. [3] x. 167 and 241.)

ALOUCHI, or **ALUCHI RESIN** is imported from Madagascar, where it is obtained, according to Valmont de Bomare, from a tree called Timpi. According to others, from *Wintera aromatica.* It is friable, whitish on the outside, black within, has a marbled appearance, and a strongly aromatic, peppery, bitter taste. According to Bonastre (J. Pharm. x. 1), it contains 68·12 p. c. of resin easily soluble in cold alcohol, 20·45 of resin sparingly soluble in cold alcohol, 1·58 essential oil, together with small quantities of free acid and ammonia-salt, besides earthy impurities. The sparingly soluble resin appears to be of peculiar nature.

ALPHENE, SULPHIDE OF. (See SULPHOCYANIDE OF AMMONIUM.)

ALSTONITE. A mineral having the same composition as *barytocalcite*, $CO^3.BaCa$. [or $BaO.CO^2 + CaO.CO^2$], but crystallising in oblique prisms, whereas baryto-calcite forms right rhombic prisms: hence carbonate of barium and calcium is dimorphous. Alstonite is found on Alston Moor in Cumberland.

ALTAITE. (See TELLURIDE OF LEAD.)

ALTHEIN. Syn. of ASPARAGIN.

ALTHIONIC ACID. $C^2H^6SO^4$.—This acid, isomeric with ethylsulphuric or sulphovinic acid, is produced, according to Regnault (Ann. Ch. Phys. [2] lxv. 98), when alcohol is heated with excess of strong sulphuric acid till olefiant gas begins to be evolved (between 160° and 180° C.) When equal parts of sulphuric acid and alcohol are used, nothing but sulphovinic acid is formed, and even in the residues of the ether-preparation on the large scale, the latter is the only acid found.

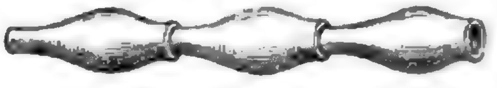
To prepare the barium-salt of althionic acid, the residue obtained in the preparation of olefiant gas from 6 pts. sulphuric acid and 1 pt. alcohol, is saturated with milk of lime; the filtrate, after evaporation, is treated with oxalic acid to precipitate the lime; the liquid again filtered and saturated with baryta-water; the excess of baryta precipitated by carbonic acid; and the filtrate evaporated, first by heat, and finally in vacuo, crystallisation then taking place as soon as the liquid acquires a syrupy consistence. The salt when purified by recrystallisation, forms spherules composed of small needles permanent in the air, and giving off 8·59 p. c. (1 at.) of water in vacuo. The formula of the crystallised salt is $C^2H^5BaSO^4 + H^2O$. It is more soluble in water than the sulphovinate of barium, and dissolves also in alcohol especially when hot.

From the aqueous solution of the barium-salt, the free acid (the hydrogen-salt) may be obtained by precipitating the baryta with sulphuric acid, and from this the other salts may be prepared by direct combination. The *calcium*-salt evaporated at the gentlest possible heat, solidifies completely in a mass, without crystallising. The *copper*-salt forms pale green, very thin rhombohedrons, having an acute angle of 60°. (Regnault.)

Magnus (Pogg. Ann. xlvii. 523) was not able to find althionic acid in the residues of the preparation of olefiant gas, but only ethionic, isethionic, and sometimes also sulphovinic acid.

ALUDELS. Pear-shaped earthern vessels used by the older chemists for subliming. They are open at each end and fit into one another in the manner shown in *fig.* 7. At the quicksilver works at Almaden in Spain, vessels of this shape are used to condense the mercurial vapours issuing from the retorts. For this purpose they are laid in the form of a chain on a slightly inclined surface called the *aludel-bath.* (See MERCURY.)

Fig. 7.



ALUM. (See SULPHATES.)

ALUMINATES. Compounds of alumina with the stronger bases.

ALUMINITE. A basic sulphate of aluminium, $Al^2O^3.SO^3 + 9HO$, found native at New Haven in America. It is a white, opaque, earthy mass, of specific gravity 1·705, soluble in hydrochloric acid. Gives off its acid at a red heat. (Stromeyer.)

ALUMINIUM. *Symbol*, Al; *Atomic weight*, 13·75.—This metal occurs in a great variety of forms, viz. as oxide (alumina) anhydrous, and hydrated, sometimes alone, but more generally associated with the oxides of other metals, iron zinc, glucinum, magnesium, &c.;—as sulphate and phosphate; as silicate, which is the chief constituent of all clays, and in combination with other silicates, forms a vast number of minerals, especially the felspars; also as mellitite, or honeystone, as fluoride of aluminium and sodium in cryolite; and in very small quantities in plants.

Alumina was first shown to be a distinct earth by Marggraff in 1754, having been previously confounded with lime. Oerstedt, in 1826, showed how to prepare the chloride of aluminium by passing chlorine over a red-hot mixture of alumina and charcoal; and Wöhler, in 1828 (Pogg. Ann. xi. 136) succeeded in eliminating the metal by igniting the chloride with potassium. It was thus obtained in the form of a grey powder intermixed with tin-white globules arising from partial fusion. It has lately been obtained in the compact form, and in much larger quantity, by H. Sainte-Claire Deville and others.

Preparation.—The mode of preparation now adopted is the same in principle as that of Wöhler, depending on the action of sodium at a red heat on the chloride or fluoride of aluminium, or better, on the double chloride or double fluoride of aluminium and sodium. Sodium is used to effect the reduction in preference to potassium, partly because it acts more regularly and with less violence, and partly because it is more easily prepared, and, having a lower atomic weight than potassium, a smaller quantity of it suffices for a given amount of chemical work.

The process first adopted by Deville consisted in passing the vapour of chloride of aluminium over sodium contained in a tube of iron or copper which was kept at a dull red heat. Metallic aluminium was thus obtained, mixed with chloride of aluminium and sodium. The latter was removed by washing with water, and the metallic globules which remained were made to unite by heating them till they began to melt, and pressing them together with a pipe-stem. The mass thus obtained was then remelted and cast into bars. Another method which promised to yield good results, but has not yet been perfected, was to reduce the chloride of aluminium by vapour of sodium. The mixture of carbonic oxide and sodium-vapour produced by heating a mixture of charcoal and carbonate of sodium (see SODIUM) was conveyed into a large earthen crucible by means of an iron tube passing through a hole near the bottom and reaching nearly to the other side; and as the sodium and carbonic oxide burned and thereby heated the crucible, portions of chloride of aluminium were thrown in from time to time. The crucible when cold was broken, and the aluminium separated from the saline mass in the manner above described.

The quantity of compact aluminium obtained by these methods was however considerably below the theoretical amount, a large portion of the metal being reduced in the form of a fine powder which re-fused to unite into globules. This inconvenience may be obviated and much better results obtained by the use of fluor spar or cryolite as a flux. These fluorides assist the union of the particles, apparently by dissolving small quantities of alumina—produced by moisture adhering to the chloride,—which surround the particles of metal at the moment of reduction, and, not being decomposed by the sodium, prevent them from uniting into globules. The reduction may be performed in crucibles, or better, in a reverberatory furnace.

a. 400 parts of chloride of aluminium and sodium, 200 pts. of chloride of sodium, 200 pts. of fluor spar or cryolite—the latter being preferable—all perfectly dry and finely pulverised, are placed together, with 75 or 80 pts. of sodium, in alternate layers, in an earthen or iron crucible, which is moderately heated till the action begins, and afterwards to redness, the melted mass being stirred with an iron rod and afterwards poured out. If the process goes on well, 20 pts. of aluminium are thus obtained in a compact mass, and about 5 pts. more in globules encrusted in a hard mass.

The aluminium thus obtained is, however, somewhat contaminated with silicon, derived from the earthy matter of the crucible, which is attacked by the sodium, by the aluminium itself, and by the fluorides in the slag. This evil may be corrected to a certain extent, but not completely, by lining the crucible with a paste composed of calcined alumina, or aluminate of calcium. If iron crucibles are used, the aluminum is found to contain iron.

b. The reduction is performed with greater facility, and on a much larger scale, by heating the mixture on the hearth of a reverberatory furnace.

The proportions used are:

Chloride of aluminium and sodium	10 parts.
Fluor spar or cryolite	5 „
Sodium	2 „

The double chloride and the cryolite or fluor spar are mixed in the state of powder with sodium in small ingots, and the whole is thrown on the hearth of the furnace previously raised to the required temperature. The dampers are then closed to prevent access of air. A vivid action soon takes place, accompanied by evolution of heat, sufficient to raise the walls of the furnace and the mixture itself to bright redness; and the mixture is almost completely liquefied. When the reduction is complete, the fused mass is run out through an aperture at the back, the slag escaping first, and then the aluminium flowing out in a single jet, and collecting in one mass below the liquid slag. With a furnace having a hearth about 16 square feet in surface, about

16 lbs. of aluminium may be obtained at one operation. The slag consists of two layers, the upper containing a large quantity of common salt, while the lower, which is pasty and less fusible, consists chiefly of fluoride of aluminium. On pulverising this latter and passing it through a sieve, an additional quantity of aluminium is obtained in globules. The fluoride of aluminium may be used for the preparation of alumina.

This process (which has been patented by MM. Rousseau, Frères and M. Paul Morin, both in France and in this country, 1856, No. 1810) is peculiarly advantageous in this respect, that the reduced metal is very little exposed to contamination with silicon. The introduction of this impurity generally arises from the action of the sodium or of the slag on the earthy matters of the vessels in which the reduction takes place. Now, when crucibles are used and the heat is applied from below, the part of the mixture in contact with the crucibles is necessarily the hottest, and consequently the action exerted on the crucible is considerable; but when the mixture is fused on the hearth of a reverberatory furnace, with the flame playing on its surface, the coolest part is in contact with the hearth, which is therefore less acted upon. Moreover with the proportions above given, the whole of the fluorine is separated as fluoride of aluminium, a compound which exerts but little action on silicious substances.

Preparation from Cryolite.—The pulverised mineral is mixed with half its weight of common salt, and the mixture is arranged in alternate layers with sodium (2 pts. of sodium to 5 pts. of cryolite), in an earthen or iron crucible, a layer of pure cryolite being placed at top, and the whole covered with common salt. The mass is rapidly heated till it melts completely, and then left to cool after being stirred with an iron rod. The aluminium is generally found in large globules. Such was the method originally practised by Professor H. Rose in Berlin, and by Dr. Percy and Mr. Allen Dick in this country. It is now carried on, on the manufacturing scale, at Amfreville, near Rouen, by C. and A. Tissier.

A peculiar apparatus for effecting the reduction of aluminium, either from the double chloride or from cryolite, the object of which is to prevent loss of sodium by ignition, has been invented and patented by F. W. Gerhard (1858, No. 2247). It consists of a reverberatory furnace having two hearths, or two crucibles or reverberatory furnaces placed one above the other, and communicating by an iron pipe. In the lower is placed the mixture of sodium with the aluminium-compound, and in the upper a stratum of chloride of sodium, or of a mixture of sodium and cryolite, or of the slag obtained in a former operation. This layer when melted, is made to run into the lower furnace in quantity sufficient to cover completely the mixture contained therein, so as to protect it from the air.

The chief inducement for using cryolite as a source of aluminium, is that it is a natural product obtained with tolerable facility, and enables the manufacturer to dispense with the troublesome and costly preparation of the chloride of aluminium and sodium. But the aluminium thus obtained is less pure than that prepared from the double chloride by the method previously described. If earthen crucibles are used, the aluminium is contaminated with silicon, because the fluoride of sodium produced by the decomposition acts strongly on the silicious matter of the crucible; and if crucibles of iron are used, the aluminium takes up a portion of that metal. For these reasons, Deville is of opinion, that the best use of cryolite is as a flux in the preparation of aluminium from the double chloride. In that case, as already observed, the slag consists, not of fluoride of sodium, but of fluoride of aluminium, which acts but slightly on the containing vessel.

Reduction of aluminium by means of hydrogen or carbon.— Several attempts have been made, but with doubtful success, to separate aluminium from its compounds by means of the ordinary reducing agents.

F. W. Gerhard decomposes fluoride of aluminium, or the double fluoride of aluminium and potassium or sodium, by subjecting it to the action of hydrogen gas at a red heat. The aluminium-compound is placed in a number of shallow dishes of glazed earthenware, each of which is surrounded by a number of other dishes containing iron filings. These dishes are placed in an oven previously heated to redness; hydrogen gas is then admitted, and the heat increased. Aluminium is then separated, and hydrofluoric acid evolved, which is immediately taken up by the iron filings, and thereby prevented from acting on the aluminium. To prevent the pressure of gas from becoming too great, an exit-tube is provided, which can be opened or closed at pleasure by means of a stopcock. This process, which was patented in 1856 (No. 2980), is ingenious and was said to yield good results; the inventor has however since returned to the use of the more costly reducing agent, sodium (see above), which would seem to imply that the hydrogen method has not quite fulfilled his expectations.

Sir Francis C. Knowles has patented a process (1857, No. 1742) for reducing aluminium from its chloride by means of cyanide of potassium or cyanide of sodium, the chloride, either in the fused state or in the form of vapour being brought in contact either with the melted cyanide or its vapour. Pure alumina may be added to increase the product.

L. F. Corbelli, of Florence, states that aluminium may be obtained by mixing the impure sulphate (prepared by heating clay with strong sulphuric acid), with 2 pts. of ferrocyanide of potassium, and 1½ pt. common salt, and heating the mixture to whiteness. The metal thus obtained must however be very impure, perhaps consisting chiefly of iron. The process was patented in this country in 1858 (No. 142).

M. Cumenge, of Paris, obtains aluminium from the sulphide (Al^4S^3) either by heating that compound in an atmosphere of hydrogen, or by heating it with alumina or sulphate of aluminium, in such proportion that the oxygen contained in that compound shall be just sufficient to convert the whole of the sulphur into sulphurous anhydride:

$$Al^4S^3 + 2Al^4O^3 = 3SO^2 + 12Al$$

$$\text{or} \quad Al^4S^3 + Al^4(SO^4)^3 = 6SO^2 + 8Al;$$

or, lastly, by decomposing the sulphide with an ordinary metal, such as iron, copper or zinc. This process is also patented (1858, No. 461).

Preparation of Aluminium by Electrolysis.—The electrolytic reduction of aluminium may be performed either in the dry or in the wet way. The reduction from fused chloride of aluminium and sodium was first effected in this manner by Bunsen in 1854 (Pogg. Ann. xcii. 648). The salt is introduced in a fused state into a red-hot porcelain crucible, divided into two parts by a porous earthenware diaphragm, and the extremities of the carbon poles of a Bunsen's battery of ten elements are introduced into the two halves of the fused mass. The metal is then reduced at the negative pole. The heat must be raised considerably above the melting-point of the double chloride, otherwise the aluminium separates in the pulverulent form. It is best to add fresh quantities of chloride of sodium during the reaction, and to raise the temperature ultimately to the melting point of silver. The aluminium is then obtained in globules of considerable size, which may be melted into one by throwing them into chloride of sodium melted at a white heat. Deville adopts a similar method, using, however, platinum instead of charcoal for the negative pole.

The same method may be used for coating metals with aluminium. Thus, if a bar of copper be used as the negative pole, and a bar of aluminium as the positive pole, tha latter dissolves as the action goes on, and is deposited upon the copper.

Aluminium may also be reduced by the action of the current from the solution of its salts. Mr. Gore has in this way obtained a deposit of aluminium on copper, and Messrs. Evans and Tilley have patented a process (1855, No. 2756), for coating metals with aluminium and its alloys, by electrolysing a solution of alumina mixed with cyanide of potassium, the negative pole being formed of the metal to be coated, and the positive pole of platinum or aluminium, or of some other metal, such as copper, tin or silver, which is to be deposited together with the aluminium. The bath may also in some instances be composed of a mixed solution of aluminium and the other metal to be deposited.—M. Corbelli, of Florence, obtains a deposit of aluminium by electrolysing a mixture of rock-alum or sulphate of aluminium with chloride of calcium or chloride of sodium, the positive pole being formed of iron wire coated with an insulating material and dipping into mercury placed at the bottom of the solution, and the negative pole of zinc immersed in the solution. Aluminium is then deposited on the zinc, and the chlorine eliminated at the positive pole unites with the mercury, forming calomel. This process is also patented (1858, No. 507).

Of all the processes above described, the only one that has been successfully applied to the production of aluminium on the large scale, is the decomposition of the double chloride or of cryolite by sodium. The electrolytic method is too expensive, excepting for producing a thin coating of aluminium on other metals; and the attempts which have been made to obtain aluminium by means of the ordinary reducing agents, such as hydrogen and charcoal, do not appear to have led to very satisfactory results. At present, therefore, the progress of the aluminium manufacture depends essentially on the economical production of sodium; and indeed the manufacture of aluminium has already given a great stimulus to that of sodium, and has led to considerable improvements in that process, and consequent reduction of cost. (See SODIUM.) *

Purification.—Aluminium may be purified from *copper* and *iron* by fusion with nitre in an iron crucible, the foreign metals being thereby oxidised, while the aluminium remains

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* When Deville commenced his experiments in 1854, great hopes were entertained that aluminium might be produced at a price sufficiently low to admit of a variety of useful applications. Hitherto these expectations have been but imperfectly fulfilled, the metal being still too costly to be applied to other than ornamental purposes. Still, however, great progress has been made, the price, which in 1856 was 3l. per oz., being now reduced to 5s.; and further reduction will doubtless be made as the details of the manufacture are improved.

intact. Before introducing the aluminium, the inner surface of the crucible should be well oxidised by the action of the nitre. Aluminium containing zinc, may be freed from that metal by melting the alloy in contact with the air. No method has yet been discovered of purifying aluminium from *silicon*.

Aluminium is very apt to retain portions of the slag in the midst of which it has been formed, causing the surface, when worked and polished, to exhibit a number of points of inferior lustre, which gradually became more and more conspicuous. The best mode of purification is to melt the metal in an open black lead crucible for a considerable time, then remove it from the fire and stir it with an iron skimmer oxidised on the surface. By this means, the whitish slaggy matter is removed, together with a small portion of the aluminium, which may be set aside to be remelted. The metal is then cast into bars, and the whole operation repeated three or four times.

[For further information respecting the preparation of aluminium, see *De l'Aluminium*, par H. Sainte-Claire Deville, 8vo. Paris, 1859; *L'Aluminium et les Metaux Alcalins*, par C. et A. Tissier, 12mo. Paris et Rouen, 1858; *Chemical Technology*, by Richardson and Watts, vol. i. pt. iv. p. 1; *Ure's Dictionary of Arts, Manufactures and Mines*, vol. i. p. 120.]

Properties.—Aluminium is a white metal, with a faint tinge of blue. It takes a fine polish, and its surface may be frosted, like that of silver, by plunging it for an instant into a very weak solution of caustic soda, washing with a large quantity of water, and then digesting it in strong nitric acid. When pure, it is quite destitute of taste and odour. It is very malleable and ductile; may be beaten and rolled as easily as gold and silver, and drawn out into extremely thin wire. In this last operation, however, it becomes very brittle, and requires to be tempered by cautiously heating it over a lamp. In elasticity and tenacity, it is about equal to silver. After fusion it is as soft as pure silver; but after hammering in the cold, it acquires the hardness of soft iron It is highly sonorous, a bar of the metal suspended by a thread and struck with a hard body, emitting a beautifully clear, ringing sound. It is very light, being not much more than 2½ times as heavy as water, and about 4 times lighter than silver. Its density after fusion is 2·56, and after being hammered in the cold, 2·67. Its melting-point is intermediate between the melting-points of zinc and silver, but nearer to the former. It may be cast with the greatest ease in metallic moulds, and still better in moulds of sand. It may be fused without any flux; indeed, the addition of a flux is rather detrimental than otherwise, the metal attacking borax and glass with facility. Aluminium, heated in a closed vessel, does not exhibit the slightest tendency to volatilise.

The electric conducting power of aluminium is eight times as great as that of iron, and about equal to that of silver; it conducts heat even better than silver. Its specific heat is very great, and hence, though its melting-point is comparatively low, it takes a long time to liquefy. The melting together of small pieces of the metal may be facilitated by shaking the crucible and pressing them together with an iron rod oxidised on the surface. When slowly cooled from fusion, it exhibits a crystalline structure; the crystallisation is, however, most distinct when the metal is impure. Aluminium precipitated from its solutions by electrolysis at low temperatures, crystallises in octahedrons, which appear to be regular. It is slightly magnetic.

Aluminium does not oxidise in the *air*, even at a strong red heat; neither does it, in the compact state at least, decompose water, excepting at a white heat, and even then but slowly (Deville). It is not attacked by *sulphuretted hydrogen*, or even by *sulphide of ammonium*, and consequently preserves its lustre in the atmosphere of large towns, where silver is very soon tarnished and blackened. It may also be heated to redness in *vapour of sulphur* without showing any disposition to combine; at very high temperatures, however, combination takes place.

Aluminium is not attacked by *nitric acid*, either dilute or concentrated, at ordinary temperatures, and very slowly even at the boiling heat; neither is it acted upon by *sulphuric acid* diluted to the degree at which that acid dissolves zinc; but *hydrochloric acid*, either dilute or concentrated, dissolves it readily, even at low temperatures, with evolution of hydrogen. The *vegetable acids*, such as acetic and tartaric acid, exert no perceptible action on aluminium; a mixture of acetic acid and common salt exerts a somewhat greater action, because it contains free hydrochloric acid; but even in this case the action is very slow, and not nearly so great as would be exerted upon tin under similar circumstances. Aluminium would therefore be well adapted for culinary vessels, especially as the small quantity of alumina which might be formed from it by the action of certain acid mixtures would not exert any deleterious action on the animal economy.

The *hydrates of potassium* and *sodium* in the state of fusion do not act upon aluminium, but their aqueous solutions dissolve it readily, forming aluminate of potassium or sodium, and giving off hydrogen. Ammonia acts but slightly on it.

A solution of *common salt* or *chloride of potassium* is also without action on aluminium, but the solutions of many other chlorides dissolve it, and more readily, as the metals which they contain are higher in the scale; even a solution of chloride of aluminium dissolves the metal, forming a basic chloride. Solutions of *sulphates* and *nitrates*, on the contrary, do not act upon it. Hence in precipitating other metals upon aluminium by electrolytic action, it is necessary to use acid solutions not containing hydrochloric acid or any chloride. In an acid solution of sulphate of copper, the aluminium quickly becomes coated with metallic copper.

Aluminium may be fused with *nitre* at a moderate heat, without undergoing the slightest alteration; hence this process may be adopted for purifying aluminium from admixtures of other metals. If however the heat be raised till the nitric acid is completely decomposed and begins to give off nitrogen, a new reaction takes place attended with incandescence, and aluminate of potassium is formed.

Uses.—The lustre and whiteness of this metal, its unalterability in the air, and the facility with which it takes a frosted surface, render it well adapted for jewellery, for which purpose it is now much used. It also makes very bright reflectors. Its lightness renders it useful for mounting astronomical instruments, especially sextants. It may also be used for making small weights, such as the divisions of the gramme. Very delicate balance-beams have also been constructed with it. For culinary vessels it is adapted by its lightness and the little tendency which it has to become corroded by any of the liquids likely to come in contact with it. It is necessary however to observe, that this power of resisting the action of corroding agencies, and more especially those of the atmosphere of large towns, is exhibited only by the pure metal. Now, much of the aluminium of commerce is very impure, being contaminated with iron or silicon, or not having been properly freed from slag. Aluminium thus contaminated soon becomes tarnished, and much disappointment has been experienced from this cause by many who have used it for ornamental purposes. According to Deville, the impurities just mentioned are found to the greatest amount in the metal obtained from cryolite (p. 152).

General Characters and Reactions of Aluminium-compounds.—Aluminium forms only one class of salts, and into these it is supposed to enter as a sesqui-equivalent radicle, 2 atoms of aluminium taking the place of 3 atoms of hydrogen: $Al^2 = H^3$, or $Al^{\frac{2}{3}} = H$. Thus, the chloride of aluminium is $(Al^2)'''Cl^3$; the oxide (alumina) is $\left.\begin{matrix}(Al^2)''' \\ (Al^2)'''\end{matrix}\right\}O^3$; the sulphate, $(Al^4)^{vi}.3SO^4$, or $\left.\begin{matrix}(3SO^2)^{vi} \\ (Al^4)^{vi}\end{matrix}\right\}O^6$, &c. These formulæ are based upon the isomorphism of the aluminium-compounds with other compounds of corresponding character, which are known or supposed to contain sesqui-equivalent radicles: thus, alumina, the only known oxide of aluminium, is isomorphous with sesquioxide of iron and sesquioxide of chromium; and common potash-alum $(Al^2)'''K'(SO^4)^2 + 12H^2O$, is isomorphous with iron-alum $(Fe^2)'''K'.(SO^4)^2 + 12H^2O$, and chrome-alum $(Cr^2)'''K'.(SO^4)^2 + 12H^2O$. All these formulæ may, however, be reduced to others containing mono-equivalent radicles, the values of which are two-thirds of those of the corresponding sesqui-equivalent radicles. For instance, the aluminium-compounds may be supposed to contain a radicle (*aluminicum*), $al = \frac{2}{3}\,Al = \frac{2}{3}\,.\,13{\cdot}75 = 10{\cdot}31$. The formula of the chloride will then be $alCl$; that of alumina, al^2O; that of the sulphate al^2SO^4; that of alum, $alK.SO^4$. It is sometimes convenient to write the formulæ in this manner.

Most compounds of aluminium are colourless. The oxide, hydrates, borates, phosphates, arseniates, and silicates, are insoluble in water; most other aluminium-compounds are soluble. All of these, excepting the silicates, are soluble in hydrochloric and sulphuric acid, at least if they have not been strongly ignited.

The aqueous solutions have an acid reaction, and an astringent disagreeable taste. They are not precipitated by any free acid. With *sulphide of ammonium* and other soluble sulphides, they give a white gelatinous precipitate of trihydrate of aluminium, the formation of which is attended with evolution of hydrosulphuric acid gas. The precipitate is insoluble in excess of that reagent, but soluble in caustic potash or soda. With solution of *potash* or *soda*, the same gelatinous precipitate of the hydrate is produced, soluble in excess of the alkali, and reprecipitated by boiling with sal-ammoniac, or by cautious neutralisation with hydrochloric acid.—With *ammonia*, the same precipitate, insoluble in excess.—With *alkaline carbonates*, the same, carbonic acid being given off, and not entering into combination with the alumina.—With *ferrocyanide of potassium*, a white gelatinous precipitate, after some time.—With *phosphate of sodium*, gelatinous precipitate, closely resembling the hydrate in appearance, and dissolving with the same facility in hydrochloric acid and in potash. From these solutions it is precipitated in the same manner as the hydrate, viz. from the hydrochloric acid solution by ammonia, and from the potash-solution by sal-ammoniac; it is distinguished from the hydrate however, by its insolubility in acetic acid, and by exhibiting certain reactions of phosphoric acid (*q. v.*)

Most compounds of aluminium, when moistened with a small quantity of *nitrate of cobalt*, and ignited before the blowpipe, exhibit a fine characteristic blue colour. This character is best exhibited by placing a small quantity of alumina, precipitated as above, on charcoal or platinum-foil, heating it to redness, then moistening with nitrate of cobalt, and igniting again.

Quantitative Estimation of Aluminium.—Aluminium is usually precipitated in the form of hydrate by excess of ammonia or carbonate of ammonium, or better by sulphide of ammonium, because an excess of ammonia or its carbonate dissolves a small but perceptible quantity of the hydrate, which can then be reprecipitated only by boiling the liquid till every trace of ammonia is expelled. The precipitate when ignited leaves anhydrous alumina, containing 53·26 per cent. of the metal.

Aluminium may also be very conveniently separated from its solutions by boiling with *hyposulphite of sodium;* alumina is then precipitated together with sulphur, while sulphurous acid is expelled, and a sodium-salt of the acid previously combined with the alumina remains in solution: thus, if the aluminium exists in solution as sulphate:

$$S^3O^{12}Al^4 + 3S^2O^3Na^2 = Al^4O^3 + 3S + 3SO^2 + 3SO^4Na^2.$$

The liquid should be dilute, and must be boiled till it no longer smells of sulphurous acid; the alumina then separates quickly in a compact mass, not at all gelatinous, and very easy to wash. The sulphur mixed with it is very easily expelled by ignition. (G. Chancel, Compt. rend. xlvi. 987.)

This mode of precipitation by hyposulphite of sodium, serves also to separate aluminium from many metals, especially from iron, the latter metal being reduced to the state of protoxide, and remaining in solution as a sodio-ferrous hyposulphite. To ensure complete separation, the solution must be nearly saturated, if necessary, with an alkaline carbonate, diluted to a considerable extent, and mixed with the hyposulphite while cold; otherwise the alumina separates too quickly, before the iron is completely reduced to protoxide, and then carries some of the iron down with it. After the separation of the alumina, the iron is re-oxidised by nitric acid and precipitated by ammonia. (Chancel.)

Aluminium may also be separated from the *alkalis* and *alkaline earths*, by precipitation with ammonia or sulphide of ammonium. In thus separating it from the alkaline earths, however, care must be taken to protect the solution from the air, otherwise carbonic acid will be absorbed by the excess of ammonia, and will precipitate the alkaline earth together with the alumina. From *barium*, aluminium is most easily separated by sulphuric acid.

Alloys of Aluminium. Aluminium forms alloys with most metals. With *zinc* and *tin* it unites readily, forming brittle alloys; with *cadmium* it forms a malleable alloy. With *iron*, aluminium unites in all proportions, forming alloys which are hard, brittle, and crystallise in long needles, when the proportion of iron amounts to 7 or 8 per cent. Aluminium containing iron dissolves in acids more readily than the pure metal. (Deville.)

Aluminium alloyed with even a small proportion of *silver*, loses all its malleability. An alloy containing 5 per cent. of silver may, however, be worked like the pure metal, and has been used for making knife-blades. An alloy containing 3 per cent. of silver is used for casting ornamental articles. It has the colour and lustre of silver, and is not tarnished by sulphuretted hydrogen. (Deville.)

The alloys of aluminium and *copper* are of especial importance. One in particular, containing 10 pts. of aluminium with 90 pts. of copper, called *aluminium-bronze*, possesses very remarkable properties. It is a definite compound, containing Cu^4Al. It has the colour of gold, takes a high polish, is extremely hard, and possesses a tenacity equal to that of the best steel; it is also very malleable. Another alloy containing only 2 or 3 per cent. of copper, is used for casting ornamental articles of large dimension, intended to be chased. Aluminium may be easily plated on copper. The plates of the two metals are prepared in the usual manner, and well rubbed with sand, then placed between two plates of iron, the whole being well bound together, heated to low redness, and then strongly pressed. (Deville.)

Alloys of aluminium may be prepared by heating a mixture of alumina and the oxide of another metal, such as copper, iron, or zinc, or a mixture of alumina with carbon and the other metal in the free state, granulated copper, for instance, the materials being all very finely divided, and mixed in atomic proportions; or rather with the carbon slightly in excess. This method, due to a foreign inventor, has been patented in this country in the name of E. L. Benzon (1858, No. 2753).

Amalgamation and Gilding of Aluminium.—According to Cailletet, aluminium may be amalgamated by the action of ammonium-amalgam or sodium-amalgam and water, also when it is connected with the negative pole of the voltaic battery, and dipped into the mercury moistened with acidulated water, or into nitrate of mercury.—Ch. Tissier (Compt. rend. xlix. 56), confirms this statement respecting the amalgamation of aluminium in connection with the negative pole of the battery, and adds, that if the aluminium foil is not very thick, it becomes amalgamated throughout, and very brittle. The same chemist finds that aluminium may be made to unite with mercury, merely by the use of a solution of caustic potash or soda, without the intervention of the battery. If the surface of the metal be well cleansed and moistened with the alkaline solution, it is immediately melted by the mercury and forms a shining amalgam on the surface.

The amalgam of aluminium instantly loses its lustre when exposed to the air, becoming heated and rapidly converted into aluminium and metallic mercury. It decomposes water, with evolution of hydrogen, formation of alumina, and deposition of mercury. Nitric acid attacks it with violence. (Tissier.)

To *gild* aluminium, 8 grammes of gold are dissolved in aqua regia, the solution is diluted with water and left to digest till the following day, with a slight excess of lime; after being well washed, it is treated at a gentle heat with a solution of 20 grms. of hyposulphate of sodium. The filtered liquid serves for the gilding of aluminium, without the aid of heat or electricity, the aluminium being simply immersed in it, after having been well cleaned by the successive use of potash, nitric acid, and pure water. (Tissier.)

It is somewhat difficult to *solder* aluminium, partly because no flux has yet been found that will clean the surface without attacking either the aluminium or the solder, partly because the surface of the aluminium is not easily melted by metals more fusible than itself. An imperfect soldering may indeed be effected by means of zinc or tin, but a better method, devised by M. Hulot, is to coat the aluminium with copper, by the electrolytic method, and then solder in the ordinary way. (Deville.)

Arsenide of Aluminium. (See ARSENIDES.)

Boride of Aluminium. Boron unites with aluminium under the same circumstances as silicon (p. 160), and alters its properties in a similar manner.

Bromide of Aluminium, Al^2Br^3, is obtained by the action of bromine on pulverulent aluminium, the metal being in excess. By sublimation, it is obtained in white, shining laminæ, which melt at 90°, forming a mobile liquid which boils at about 265° C. It is decomposed when heated in contact with the air. It dissolves in bisulphide of carbon, forming a solution which fumes strongly in the air. It dissolves in water, and the solution evaporated in vacuo over oil of vitriol, leaves needle-shaped crystals containing $Al^2Br^3 + 6H^2O$. With bromide of potassium, it forms the double salt $KBr.Al^2Br^3$. It absorbs ammonia and hydrosulphuric acid, forming compounds which are decomposed by heat. (R. Weber, Pogg. Ann. ciii. 254.)

Chloride of Aluminium, Al^2Cl^3.—The finely divided metal heated to redness in a current of dry chlorine gas, takes fire and is converted into the chloride, which sublimes (Wöhler). The compound is also produced by passing dry chlorine over an ignited mixture of alumina and charcoal: and this is the method adopted for preparing it. Hydrate of aluminium precipitated from a hot solution of alum by an alkaline carbonate is made up into small pellets with oil and lampblack, and the mixture is strongly ignited in a crucible: the oil is then decomposed and an intimate mixture of alumina and charcoal remains. This is introduced into a porcelain tube or tubulated earthen retort placed in a furnace, and connected at one end with an apparatus for evolving chlorine, and at the other with a dry receiver. On raising the heat to bright redness, and passing chlorine through the apparatus, chloride of aluminium is formed and condenses in a solid mass in the receiver.

A similar process is adopted in preparing the compound on the large scale. Alumina or clay is mixed with coal, pitch, tar, resin, or any organic substance that will decompose by heat and leave a considerable quantity of charcoal, and the mixture, after being well calcined, is heated to redness in a cylinder of earthenware or cast iron, through which a current of dry chlorine is made to pass. The vapours of chloride of aluminium pass into a condensing chamber lined with plates of glazed earthenware, on which the chloride collects in the solid state. If clay containing a considerable proportion of iron is used in the preparation, it must first, after ignition with carbonaceous matter — whereby the iron is reduced to the metallic state — be treated with a dilute acid to dissolve out the iron, then washed and dried.

Chloride of aluminium is a transparent waxy substance having a crystalline structure like talc. It is colourless when pure, but generally exhibits a yellow colour, due perhaps to the presence of iron. It is fusible in large masses, and according to Liebig, boils at about 180° C. A small quantity volatilises immediately when heated. It fumes in the air, and smells of hydrochloric acid. It is decomposed at a heat below redness by potassium or sodium, aluminium being set free. When it is distilled with sulphuric anhydride, sulphurous anhydride and chlorine are given off and sulphate of aluminum remains. (H. Rose.)

$$2\mathrm{Al^2Cl^3} + 6\mathrm{SO^3} = \mathrm{Al^4(SO^4)^3} + 3\mathrm{SO^2} + 6\mathrm{Cl}.$$

Chloride of aluminium is very deliquescent, and dissolves readily in water. The solution left to evaporate in a warm dry place, yields the hydrated chloride $\mathrm{Al^2Cl^3.6H^2O}$ in six-sided prisms. The same solution is formed by dissolving alumina in hydrochloric acid. The anhydrous chloride cannot be obtained by heating the hydrated chloride, because the latter is thereby resolved into alumina and hydrochloric acid.

Chloride of Aluminium and Sodium, $\mathrm{NaCl.Al^2Cl^3}$, is obtained by fusing together the component chlorides in the proper proportions; by passing the vapour of chloride of aluminium over fused chloride of sodium; or by adding the proper quantity of chloride of sodium to the mixture of alumina or aluminiferous matter and carbon used for the preparation of chloride of aluminium, and igniting the mass in an atmosphere of dry chlorine or hydrochloric acid, and condensing the vapour in the same manner as that of the simple chloride. It is a crystalline mass which melts at 200° C., and crystallises on cooling. It is perfectly colourless when pure, much less deliquescent than chloride of aluminium, and being quite fixed at ordinary temperatures, may be handled with facility. These qualities render it much more convenient than the simple chloride for the preparation of aluminium. When ignited with sodium, it yields nearly the theoretical quantity (14 p. c.) of aluminium.

Fluoride of Aluminium, $\mathrm{Al^2F^3}$, is produced by the action of gaseous fluoride of silicon on aluminium. The product is at first mixed with reduced silicon, but this may be easily removed by digestion with a mixture of hydrofluoric and nitric acids. Fluoride of aluminium then remains in a colourless mass of cubical crystals, which have but little refracting power. It volatilises at a bright red heat, is insoluble in water, and resists the action of all acids. (Deville, Compt. rend. xliii. 49.)

Fluoride of Aluminium and Potassium, $\mathrm{3KF.Al^2F^3}$, is obtained as a gelatinous precipitate by dropping a solution of fluoride of aluminium into a solution of fluoride of potassium, till the latter remains in only slight excess. A precipitate of similar character, but consisting of $\mathrm{2KF.Al^2F^3}$, is obtained by stirring up a solution of fluoride of aluminium with a quantity of fluoride of potassium not quite sufficient for complete saturation. Both precipitates dry up to white powders, and give off the whole of their fluorine as hydrofluoric acid when heated with sulphuric acid. (Berzelius.)

Fluoride of Aluminium and Sodium, $\mathrm{3NaF.Al^2F^3}$.—Found native as *Cryolite*, and prepared artificially by pouring hydrofluoric acid in excess on a mixture of calcined alumina and carbonate of sodium in the proportions indicated by the formula, then drying and fusing the mixture. Cryolite belongs to the quadratic or dimetric system. It is colourless and transparent, softer than felspar, of specific gravity 2·96, melts below a red heat, and forms an opaque glass on cooling: so likewise does the artificially prepared salt. It is found in large quantity at Evigtok in Greenland, but has not hitherto been discovered in any other locality. It is used, as already described, for the preparation of aluminium, and also in Germany for the manufacture of soda for the use of soap-boilers.

Iodide of Aluminium, $\mathrm{Al^2I^3}$, is obtained by heating the metal with iodine or iodide of silver in sealed tubes. After repeated sublimation over metallic aluminium, it forms a snow-white crystalline mass, which melts at about 185° C., and boils at a temperature above the boiling-point of mercury. It resembles the bromide in most of its properties. With water it forms the hydrate $\mathrm{Al^2I^3.6H^2O}$, which may also be obtained by dissolving hydrated alumina in hydriodic acid. It forms double salts with the alkaline iodides, and absorbs ammonia, forming a snow-white powder. It does not appear to combine with hydrosulphuric acid. (Weber, Pogg. Ann. cvii. 264.)

Oxide of Aluminium. *Alumina*, $\mathrm{Al^2O^3}$, or Al^2O^3.—This, which is the only known oxide of aluminium, is formed by the direct combination of the metal with oxygen. Aluminium in the massive state does not oxidise, even at a strong red heat; but in the state of powder it burns brightly when heated to redness in the air or in oxygen gas, and is converted into alumina, 53·3 pts. of the metal taking up 46·69 pts. of oxygen to form 100 pts. of alumina. The atomic constitution of alumina cannot be determined from this or any other direct experiment, because there is no other oxide of aluminium with which to compare it; but it is inferred to be a sesquioxide, because it is isomorphous with the sesquioxides of iron and chromium, and is capable of replacing those oxides in combination in any proportion.

Alumina occurs native, and very nearly pure, in the form of *corundum*, varieties of which, distinguished chiefly by their colour, are the *sapphire*, *ruby*, *oriental topaz*, *oriental amethyst*, &c. The colourless variety is called *hyaline corundum*. The crystalline forms of these gems all belong to the rhombohedral or hexagonal system, the primary form being a rather acute rhombohedron. Alumina in the crystalline state has a specific gravity of about 3·9, and is, next to the diamond, the hardest substance known. An opaque variety of corundum called *emery*, which has a brown red colour, arising from oxide of iron, is much used in the state of powder for polishing glass and precious stones.

Alumina is prepared artificially: 1. By precipitating a boiling solution of common alum (sulphate of aluminium and potassium), free from iron, with carbonate of ammonium, washing the precipitate with water, and igniting it to expel the combined water.—2. By igniting sulphate of aluminium or ammonia-alum. In the former case, sulphuric anhydride is given off; in the latter, that compound, together with sulphate of ammonium, and alumina remains:

$$Al^4.3SO^4 = Al^4O^3 + 3SO^3$$

$$\text{and} \qquad 2(Al^2.NH^4.2SO^4) = Al^4O^3 + (NH^4)^2.SO^4 + 3SO^3.$$

Alumina thus prepared is apt however to retain a small quantity of sulphuric acid, and if the original salt contained iron, the whole of that impurity remains in the residue.—3.* By digesting clays, felspathic rocks, or other minerals containing alumina in a strong solution of caustic potash or soda, assisting the action, if necessary, by boiling under pressure, or by heating the same minerals with kelp or soda-ash in a reverberatory furnace, and lixiviating the fused product with water. A solution of aluminate of potassium or sodium is thus obtained, a silico-aluminate of the alkali generally remaining undissolved—and the alumina may be precipitated from the solution as a hydrate by passing carbonic acid through the liquid; by treating it with acid carbonate of sodium, or with neutral or acid carbonate of ammonium; by saturating with an acid (using by preference the last vapours of hydrochloric acid evolved in the manufacture of that compound); by treating it with chloride of ammonium, whereupon, ammonia is evolved, chloride of potassium or sodium remains in solution, and alumina is precipitated; or by mixing the solution of the alkaline aluminate with chloride of aluminium, the result being the precipitation of the alumina from both compounds:

$$\underbrace{Al^2K^3O^3}_{\text{Aluminate of potassium.}} + Al^2Cl^3 = Al^4O^3 + 3KCl.$$

4. By mixing cryolite with rather more than $\frac{3}{4}$ of its weight of quick lime, adding a small quantity of water to slake the lime, then a larger quantity, and heating the mixture by a current of steam. The products of this operation are fluoride of calcium and aluminate of sodium:

$$\underbrace{Al^2Na^3F^6}_{\text{Cryolite.}} + 3Ca^2O = 6CaF + \underbrace{Al^2Na^3O^3}_{\text{Aluminate of sodium.}}$$

The aluminate of sodium is decanted from the heavy deposit of fluoride of calcium, and decomposed by carbonic acid as above. If any insoluble aluminate of calcium should be formed, it may be decomposed by digestion with carbonate of sodium. (Deville.) 5. The slag obtained in the preparation of aluminium from chloride of aluminium and sodium, with fluor-spar or cryolite as a flux (p. 150), contains about 40 per cent. of fluoride of aluminium, together with soluble chlorides; and the residue of the extraction of sodium by Deville's process (see SODIUM), which consists in igniting a mixture of carbonate of sodium, carbonaceous matter and chalk, contains about 14·5 p. c. carbonate of sodium, 8·3 p.c. caustic soda, and 29·8 p.c. carbonate of calcium. Now, by heating to redness a mixture of 5 or 6 pts. of the sodium-residue with 1 pt. of the aluminium-slag, freed by washing from the soluble constituents, and lixiviating the product after cooling, a solution of aluminate of sodium is obtained which may be decomposed by carbonic acid as above. (Deville.)

Alumina prepared by any of the preceding processes contains iron. From this it may be purified by dissolving it in caustic alkali and precipitating the iron by a stream of sulphuretted hydrogen (Deville). It may then be reprecipitated by carbonic acid. The alumina thus precipitated always contains a certain quantity of

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* This process, the invention of M. Le Chatelier of Paris, is patented in this country in the name of H. F. Newton, 1858, No. 1988, and 1859, No. 957.

alkaline carbonate, which cannot be removed by washing with water. It may, however, be separated by digestion, with the aid of heat, in a small quantity of dilute hydrochloric or nitric acid, or by digestion with chloride of aluminium in excess. (Le Chatelier.)

Artificially prepared alumina is white, and if it has been exposed only to a moderate red heat, is very light and soft to the touch; but after strong ignition, it cakes together, becomes so hard as scarcely to be scratched with a file, and emits sparks when struck with steel. According to H. Rose (Pogg. Ann. lxxiv. 430), the specific gravity of alumina ignited over a spirit-lamp is between 3·87 and 3·90; after six hours' ignition in an air furnace, it is between 3·725 and 3·75; and after ignition in a porcelain furnace, 3·999, which agrees very nearly with that of native corundum.

Alumina is infusible at all temperatures below that of the oxy-hydrogen flame; but at that degree of heat, it melts into transparent globules which assume a crystalline structure on cooling. If a small quantity of chromate of potassium be added before fusion, the melted alumina on cooling retains a deep red colour, and resembles the natural ruby. When a mixture of 1 pt. of alumina and 3 or 4 pts. of anhydrous borax is exposed for a considerable time to the high temperature of a porcelain furnace, the alumina dissolves in the fused borax, and as the borax is volatilised by the heat, remains in crystals resembling corundum; in this case also, the addition of a very small quantity of chromate of potassium causes the crystals to exhibit the colour of the ruby. This method is applicable to the artificial formation of a great number of crystallised minerals. (Ebelmen, Ann. Ch. Phys. [3] xxii. 211.)

Alumina is not decomposible by heat alone. Potassium at a white heat deoxidises it partially, forming an alloy of potassium and aluminium which decomposes water. It is not decomposed by chlorine at any temperature, unless it be mixed with charcoal, in which case a chloride of aluminium is produced.

Anhydrous alumina is perfectly insoluble in water. After strong ignition, it is likewise insoluble in most acids, concentrated hydrochloric or sulphuric acid being alone able to dissolve it. In the crystallised state it is insoluble in all acids. It may, however, always be rendered soluble by fusion with hydrate of potassium or sodium.

HYDRATES OF ALUMINIUM, OR OF ALUMINA. These compounds are three in number, viz.:

Monohydrate	Al^2HO^2	or	$Al^2O^3.HO$.
Dihydrate	$Al^4H^4O^5$	„	$Al^2O^3.2HO$.
Trihydrate	$Al^2H^3O^3$	„	$Al^2O^3.3HO$.

The monohydrate is found native as *Diaspore*, a mineral which forms translucent granular masses of specific gravity 3·43, and crumbles to powder when heated, but does not give off the whole of its water below 360° C. It is insoluble in water, and even in boiling hydrochloric acid.

The *trihydrate* is the ordinary gelatinous precipitate, obtained by treating solutions of aluminium-salts, alum, for example, with ammonia or alkaline carbonates; it is also thrown down from the same solutions by sulphide of ammonium, the aluminium not entering into combination with the sulphur. When dried at a moderate heat, it forms a soft friable mass, which adheres to the tongue and forms a stiff paste with water, but does not dissolve in that liquid. At a strong red heat, it parts with its water, and undergoes a very great contraction of volume. It dissolves with great facility in acids, and in the fixed caustic alkalis. When a solution of alumina in caustic potash is exposed to the air, the potash absorbs carbonic acid, and the trihydrate of aluminium is then deposited in white crystals which are but sparingly soluble in acids.

The trihydrate of aluminium has a very powerful attraction for organic matter, and when digested in solutions of vegetable colouring matter, combines with and carries down the colouring matter, which is thus removed entirely from the liquid if the alumina is in sufficient quantity. The pigments called *lakes* are compounds of this nature. The fibre of cotton impregnated with alumina acquires the same power of retaining colouring matters; hence the great use of aluminous salts as *mordants* to produce fast colours. (See DYEING.)

Trihydrate of aluminium occurs native as *Gibbsite*, a stalactitic, translucent, fibrous mineral, easily dissolved by acids.

Dihydrate of Aluminium, $Al^4H^4O^5$, or $Al^4O^3,2H^2O$.—When a dilute solution of diacetate of aluminium is exposed for several days to a temperature of 100° C. in a close vessel, the acetic acid appears to be set free, although no precipitation of alumina takes place. The liquid acquires the taste of acetic acid, and if afterwards boiled in an open vessel, gives off nearly the whole of its acetic acid, the alumina nevertheless remaining in solution. This solution is coagulated by mineral acids and by most vegetable acids, by alkalis, and by decoctions of dye-woods. The alumina contained in it is, however, no longer capable of acting as a mordant. Its coagulum with dye-woods has the colour of the infusion, but is translucent and totally different from the dense opaque lakes which ordinary alumina forms with the same colouring matters. On evaporating the solution to dryness at 100° C. the alumina remains in the form of dihydrate, retaining only a trace of acetic acid. In this state, it is insoluble in the stronger acids, but soluble in acetic acid, provided it has not been previously coagulated in the manner just mentioned. Boiling potash converts it into the trihydrate (Walter Crum, Chem. Soc. Qu. J. vi. 225). The dihydrate is said to occur native at Béaux (Berthier, Schw. J. xxxiv. 154). *Hydrargyllite*, a mineral occurring in regular six-sided prisms is also a hydrate of aluminium, but its exact composition is not known. (G. Rose, Pogg. Ann. xlviii. 564; l. 656.)

Aluminates.—The hydrogen in trihydrate of aluminium, may be replaced by an equivalent quantity of various metals; such compounds are called *aluminates*. According to Frémy, a solution of alumina in potash slowly evaporated [out of contact of air?] deposits granular crystals of aluminate of potassium, Al^2KO^2, or Al^4O^3, K^2O. Similar compounds occur native; thus *Spinell* is an aluminate of magnesium, Al^2MgO^2; *Gahnite*, an aluminate of zinc, Al^2ZnO^2.

Oxygen-Salts of Aluminium.—The general characters of these salts have already been described (p. 154). The most important of them are the sulphate $Al^4(SO^4)^3$, with its double sulphates, especially common alum, the sulphate of aluminium and potassium, and the silicates and double silicates. [For the detailed descriptions of these salts, see the several Acids.]

Phosphide of Aluminium.—Obtained by heating pulverulent aluminium to redness in phosphorus vapour. It is a dark grey mass, which acquires metallic lustre by burnishing, and is decomposed by water, with evolution of non-spontaneously inflammable phosphoretted hydrogen. (Wöhler.)

Silicide of Aluminium.—Aluminium combines readily, and in all proportions, with *silicon*. When strongly heated in contact with any silicious substances, such as glass or porcelain, it reduces the silicon and unites with it. Nevertheless aluminium may be fused in glass or earthen vessels, without undergoing the slightest alteration, provided no flux be used, because it does not then come into intimate contact with the substance of the vessel; but the addition of a flux produces instant decomposition. The properties of the compound vary with the proportion of silicon. An alloy containing 10·3 per cent. of silicon, called *cast* aluminium (*fonte d'aluminium*) is grey and very brittle. A compound containing 70 per cent. silicon, still exhibits metallic properties. All the compounds of aluminium and silicon are much more easily altered by exposure to the air, or by the action of acids and alkalies, than either pure aluminium or pure silicon.

Selenide of Aluminium, Al^4Se^3, or Al^2Se^3—Produced with incandescence when aluminium is heated in selenium vapour. It is a black powder, which acquires a dark metallic lustre by burnishing, and is readily decomposed by water or by a moist atmosphere, with formation of alumina and hydroselenic acid.

Sulphide of Aluminium, Al^4S^3, or Al^2S^3.—Sulphur may be distilled over aluminium without combining with it; but when thrown upon the red-hot metal, it is absorbed with vivid incandescence (Wöhler). The sulphide may be prepared by passing the vapour of disulphide of carbon over red-hot alumina. It is fusible, decomposes water at ordinary temperatures, yielding hydrate of aluminium and hydrosulphuric acid, and thus perhaps contributes to the formation of natural sulphur springs. (Frémy.)

ALUMO-CALCITE. A mineral from Erbenstock, in the Saxon Harz, having the appearance of opal. Specific gravity 2·1 to 2·2, scarcely harder than mica. Contains, according to Kersten's analysis, 6·25 per cent. lime, 2·23 alumina, and 40 water. It is probably a mere residue of decomposition.

ALUM-EARTH. A massive variety of aluminous schist, found in the neighbourhood of tertiary lignites, as in several parts of the valley of the Oder, on the Rhine, in Picardy, and other localities. It has not a distinct slaty structure, but is a soft, friable, usually dark brown mass.

ALUM-SLATE. A clay slate, containing bitumen and sulphide of iron, generally found in the transition-strata, but sometimes in more recent formations. It is found in the north of England and in Scotland, in Scandinavia, in the Harz, in the Ural, the Vosges, the lower Rhine, and other localities. There are two varieties of it, viz. 1. *Common.* This mineral occurs both massive and in insulated balls of a greyish-black colour, dull lustre, straight slaty fracture, tubular fragments, streak coloured like itself. Though soft, it is not very brittle. Effloresces, acquiring the taste of alum.

2. *Glossy Alum-slate.* A massive mineral of a bluish-black colour. The rents display a variety of lively purple tints. It has a semi-metallic lustre in the fracture,

which is straight, slaty, or undulating. There is a soft variety of it, approaching in appearance to slate clay. By exposure to air its thickness is prodigiously augmented by the formation of a saline efflioresence, which separates its thinnest plates. These afterwards exfoliate in brittle sections, causing entire disintegration.

ALUNITE, or **ALUM-STONE.** A basic sulphate of aluminium and potassium, $Al^2K.2SO^4 + 3Al^2H^3O^3$ or $\left.\begin{matrix}K^2O\\ Al^4O^3\end{matrix}\right\} 4SO^3 + 3(Al^4O^3.3H^2O)$, found chiefly in volcanic districts, viz. at Tolfa, near Civita Vecchia, at Solfatara, near Naples, at Puy de Garcey, in Auvergne, and other localities. Used for the preparation of Roman alum.

It is either massive or crystallised; the former is usually greyish white, and sometimes red. It is translucent, easily frangible, scratches calcareous spar, but is scratched by fluor spar. The crystals are generally situated in the cavities of the massive substance, they are small, shining, sometimes externally brownish, their form is an obtuse rhomboid, variously modified. The crystals have the composition above given: the massive variety contains in addition a considerable quantity of silica.

ALUNOGEN. Native sulphate of aluminium. (See SULPHATES.)

AMALGAM. A combination of mercury with another metal. (See MERCURY.)

AMALGAMATION. The process of extracting gold and silver from their ores by dissolving them out with mercury. (See GOLD and SILVER.)

AMALIC ACID (from ἀμαλός, *soft*, on account of its feeble acid reaction.)—A product of the decomposition of caffeine by chlorine (see CAFFEINE), discovered by Rochleder. Its composition is that of alloxantin, having the whole of its hydrogen replaced by methyl: $C^4(CH^3)^4N^4O^7 + H^2O$.

It forms transparent colourless crystals, which do not give off their water at 100° C. At a higher temperature, it melts and volatilises, leaving scarcely a trace of charcoal, but giving off ammonia, and yielding an oil and crystallised body. It slightly reddens litmus, and produces red stains on the skin, imparting to it an unpleasant odour, like alloxantin. It reduces silver-salts like alloxantin. Nitric acid converts it into a crystalline substance. When exposed to vapour of ammonia, it gradually assumes a deep violet colour, and forms a compound which dissolves in water with the colour of murexide: the solution yields a crystalline body, to which Rochleder gives the name *murexoin.* With baryta, potash, and soda, it forms compounds of a deep violet colour.

AMANITINE. An organic base obtained by Letellier from the fly agaric (*Agaricus muscarius*, or *Amanita muscaria*), and from *Agaricus bulbosus*, and supposed by him to be the poisonous principle of these agarics. According to Apaiger and Wiggers, on the other hand, the fly agaric contains a peculiar acid (muscaric acid), as well as a base, and it is to the acid that the poisonous action is due. (Handw. d. Chem. 2te Aufl. i. 663.)

AMARINE. $C^{21}H^{18}N^2$. *Benzoline, Pikramin, Hydrure d'azobenzoiline.*—(Laurent, Ann. Ch. Phys. [3] i. 306; Fownes, Ann. Ch. Pharm. liv. 363; Gössmann, Ann. Ch. Pharm. xciii. 329; Gm. xii. 193.)

This compound was discovered simultaneously by Laurent and by Fownes. It is isomeric with hydrobenzamide, from which it is generally prepared. 1. When hydrobenzamide is heated for three or four hours to 120°—130° C., the vitreous mass, when cool, dissolved in boiling alcohol, and excess of hydrochloric acid added, white crystals of hydrochlorate of amarine separate out (Bertagnini). — 2. Hydrobenzamide is boiled for some hours with caustic potash, the resulting resin dissolved in dilute sulphuric acid, the solution precipitated by ammonia, and the precipitate washed with water and crystallised from hot alcohol (Fownes). — 3. A solution of bitter-almond oil in alcohol, when saturated with gaseous ammonia, solidifies in 24—48 hours into a crystalline mass. This is boiled with water, and saturated while hot with hydrochloric acid, when an oily substance separates out, together with crystals of a peculiar acid (see BENZIMIC ACID). The hot solution is decanted, and the residue again extracted with boiling water, until all the hydrochlorate of amarine is dissolved out. The solution is precipitated by ammonia; and the precipitate is washed, dissolved in boiling alcohol, mixed with hydrochloric acid, and reprecipitated by ammonia: pure amarine then crystallises out (Laurent). — 4. When the dry compound of bitter-almond oil and acid sulphite of ammonium is heated in a large retort to 180°—200° with 3 or 4 times its volume of slaked lime, amarine and lophine distil over. The former, which collects partly in the receiver, partly in the lower part of the neck of the retort, is dissolved in alcohol, and purified as in the former process. (Gössmann.)

Amarine crystallises from alcohol in shining six-sided prisms. It melts at 100° C. and solidifies to a vitreous mass on cooling: when heated more strongly, it volatilises almost completely, ammonia being evolved: an oil smelling like benzol distils over, and a sublimate collects in the neck of the retort, which Fownes calls *pyrobenzoline*, and which, according to Laurent, is identical with lophine. Amarine is inodorous, tasteless at first, but afterwards slightly bitter. It is insoluble in water, soluble in alcohol and ether; the alcoholic solution is strongly alkaline. Amarine becomes strongly electrical by friction. Unlike its isomer, hydrobenzamide, it exerts a poisonous action on animals.

Amarine is readily attacked by bromine, hydrobromate of amarine being formed together with a resinous mass. When it is boiled with a mixture of sulphuric and chromic acids and water, a brisk action takes place, and benzoic acid is abundantly formed. Nitric acid acts similarly, but less violently. Fused potash does not attack it, save at a very strong heat.

Amarine-salts are formed by the direct combination of amarine with acids. With the exception of the acetate, they are all but slightly soluble. The *hydrochlorate*, $C^{21}H^{18}N^2,HCl$, crystallises in small shining needles, which effloresce in vacuo, or when heated to 100°. When hydrochloric acid is poured upon amarine, a colourless oil is formed, which gradually solidifies on drying, and may be drawn into threads when heated. It distils without decomposition, passing over as an oil which solidifies to a transparent mass. It is soluble in alcohol and ether. The *chloroplatinate* separates in yellow needles, when boiling alcoholic solutions of the hydrochlorate and of dichloride of platinum are mixed together. Fownes found in it 19·8 per cent. platinum; the formula $PtCl^2.C^{21}H^{19}N^2$ requires 19·58 per cent. The *sulphate* crystallises from an acid solution in small colourless prisms resembling oxalic acid. The *nitrate* is obtained by treating amarine with hot dilute nitric acid; a soft, amorphous mass is produced, which dissolves in boiling water, and on cooling deposits small crystals, which remain unaltered in vacuo. The *acetate* is very soluble, and yields on evaporation a gummy non-crystalline mass.

Diethylamarine, $C^{21}(C^2H^5)^2H^{16}N^2$.—Amarine heated with iodide of ethyl, yields a crystalline salt, which is the hydriodate of this base. The base itself is obtained by distilling the hydriodate with potash. It crystallises readily in oblique rhombic prisms, is nearly insoluble in water, but dissolves readily in alcohol and ether. It melts between 110° and 115° C. but does not solidify again till cooled down to 70°. At a stronger heat it decomposes. The *hydrochlorate* crystallises in oblique rhombic prisms. The *platinum-salt* is a yellow powder, insoluble in water and in ether, but soluble in alcohol, from which it crystallises in small prisms. (Borodine, Ann. Ch. Pharm. cx. 78.)

Diethylamarine treated with iodide of ethyl yields the hydriodate of another crystalline base, probably triethylamarine, which however has not yet been analysed, and this base again treated with iodide of ethyl, yields a third crystalline base. (Borodine.)

Trinitramarine, $C^{21}H^{15}(NO^2)^3N^2$ (Bertagnini, Ann. Ch. Pharm. lxxix. 275).—This compound is formed from trinitrohydrobenzamide, with which it is isomeric, just as amarine is from hydrobenzamide. Trinitrohydrobenzamide is boiled with 1 vol. caustic potash of 46° Baumé, and 50 vols. water; the resulting brown resinous mass (which becomes brittle on cooling) is dissolved in hot alcohol; a little ether added; and the solution is precipitated by hydrochloric acid. The hydrochlorate is redissolved in alcohol, alcoholic ammonia added to the solution, and the precipitated trinitramarine is washed with water, and recrystallised from alcohol. Trinitramarine is also obtained by heating trinitrohydrobenzamide in an oil-bath to 125°—130° C.

It crystallises slowly from its alcoholic solution in white hard nodules. It melts in boiling water, and dissolves slightly, forming an alkaline solution. It is soluble in boiling alcohol or ether, most readily in a mixture of the two. A hot saturated solution deposits it on cooling as an amorphous powder.

Its salts are but slightly soluble in water. The *hydrochlorate* separates in small shining needles when hydrochloric acid is added to an alcoholic solution of trinitramarine; it is nearly insoluble in cold, slightly soluble in boiling alcohol. The *nitrate* crystallises in needles from boiling alcohol. An alcoholic solution of trinitramarine forms with *dichloride of platinum*, small, yellow, heavy nodules insoluble in alcohol; and with *mercuric chloride*, a somewhat crystalline precipitate.—F. T. C.

AMARONE. $C^{16}H^{11}N$ (Laurent, Rev. Scient. xviii. 207, &c).—A compound formed by the dry distillation of azobenzoyl, benzoylazotide, or hydrobenzamide. The sublimate obtained by heating benzoylazotide is washed with ether, and then freed from lophine by boiling in alcohol containing hydrochloric acid; the residue is washed with alcohol, dried, crystallised from boiling rock-oil, and washed with ether. It forms small, colourless, inodorous needles, which melt at 233° C., and solidify to a radiated mass on cooling. It is insoluble in water, slightly soluble in alcohol, more readily in ether. It dissolves in cold sulphuric acid, with a fine blood-red colour, which disappears on addition of water, the amarone separating out. It dissolves sparingly in hot nitric acid, and crystallises unchanged on cooling. It is not decomposed by boiling with alcoholic potash.—F. T. C.

AMARYL. A name given by Laurent to a substance which he afterwards found to be impure nitrate of lophine.

AMARYTHRIN. Syn. with ERYTHRIN-BITTER or PICRO-ERYTHRIN.

AMASATIN. Syn. with ISAMIDE.

AMAUSITE. Compact FELSPAR.

AMAZON-STONE. A variety of orthoclase, coloured green by copper. It is found chiefly in the shores of Lake Ilmen in Russia, also in Norway. It is used for making trinkets.

AMBER. *Succin, Electrum, Ambra flava, Bernstein, Agtstein, gelbes Erdharz.*—A hard brittle tasteless substance, sometimes perfectly transparent, but mostly semi-transparent or opaque, and of a glassy surface; it is found of all colours but chiefly yellow or orange, and often contains leaves or insects. Its specific gravity varies from 1·065 to 1·070; hardness 2 to 2·5; slightly brittle; fracture conchoidal. It is susceptible of a fine polish, and becomes electric by friction: hence the word electricity (from ἤλεκτρον, amber). When rubbed or heated, it emits a peculiar smell. It is insoluble in water and alcohol, though the latter, when highly rectified, extracts a reddish colour from it. It is soluble in sulphuric acid, to which it imparts a reddish purple colour, but is reprecipitated on addition of water. No other acid dissolves it, nor is it soluble in essential or expressed oils without decomposition; but pure alkalis dissolve it.

According to Berzelius, amber contains a volatile oil, succinic acid, and two resins soluble in alcohol and ether. According to Schroetter and Forchammer, amber when deprived by ether of all its soluble constituents, possesses the composition of camphor viz. $C^{10}H^{16}O$.

The dry distillation of amber presents three distinct phases, characterised by the nature of the products. When submitted to the action of heat, amber softens, fuses, intumesces considerably, and gives off succinic acid, water, oil, and a combustible gas. If now the residue (*Colophony of Amber*) be more strongly heated, a colourless oil passes over. Lastly, when the residue is completely charred, and the heat is raised till the glass nearly fuses, a yellow substance sublimes of the consistence of wax.

The oil thus produced is a mixture of several hydrocarbons. The more volatile portion which passes over between 110° and 260° C., is decomposed in the cold by sulphuric acid, and coloured blue by hydrochloric acid, and by chlorine; the less volatile portion produced by a heat approaching redness, begins to boil at 140°, and then rises to 300°; sulphuric and hydrochloric acid and chlorine do not alter it. According to Pelletier and Walter (Ann. Ch. Phys. [3] ix. 89), these oils present the composition of oil of turpentine, containing 88·7 per cent. of carbon, and 11·3 of hydrogen.

The crude mixture of the two oils is used in pharmacy under the name of oil of amber, being in fact one of the constituents of *Eau de Luce*, a preparation sometimes used as a remedy for the bites of venomous animals, and consisting of 1 part of oil of amber, 24 of alcohol, and 96 of caustic ammonia.

The wax-like solid which passes over in the dry distillation of amber is a mixture of oil, yellow matter, a white crystalline substance, and a brown bituminous substance; these bodies are separated by treatment with ether and alcohol. The yellow matter appears to be identical with chrysene (C 94·4, H 5·8). It is scarcely soluble in boiling alcohol and ether, is pulverulent rather than crystalline, and requires for fusion a temperature of 240° C.

The white matter (*succisterene*) is tasteless and inodorous, it is scarcely soluble in cold alcohol, but little soluble in ether, but more soluble than the yellow matter; it melts between 160° and 162°, and distils above 300°. Nitric acid resinises it in the cold. It contains, according to Pelletier and Walter, 95·6 per cent. of carbon and 5·6 of hydrogen.

When amber is treated with fuming nitric acid, a resin is formed (artificial musk) which is soluble in an excess of nitric acid, and contains $C^{15}H^{16}N^2O^2$.

When powdered amber is distilled with a strong solution of potash, a watery liquid passes over, together with a white substance which exhibits all the properties of common camphor.

Amber occurs plentifully in regular veins in some parts of Prussia, especially between Palmnicken and Grosz-Hubenicken. In East and West Prussia there is scarcely a village where it has not been found. and thence it extends into Mecklenburg and Holstein and in fact along the whole Baltic plain. It has likewise been found in southern Germany, in France, Italy, Spain, Sweden and Norway; also on the shores of the

Caspian, in Siberia, Kamtschatka, China, Hindoostan, Madagascar, North America and Greenland. In Britain it is thrown out by the sea on the shores of Norfolk, Suffolk and Essex, and has also been found in the sands at Kensington. In the Royal Cabinet at Berlin there is a mass of 18 lbs. weight, supposed to be the largest ever found.

Haüy has pointed out the following characters by which amber may be distinguished from mellite and copal, the bodies which most closely resemble it. Mellite is infusible by heat; a bit of copal heated at the end of a knife takes fire, melting into drops, which flatten as they fall; whereas amber burns with spitting and frothing, and when its liquefied particles drop, they rebound from the plane which receives them.

Various frauds are practised with this substance. Neumann states as the common practices of workmen the two following: The one consists in surrounding the amber with sand in an iron pot, and cementing it with a gradual fire for forty hours, some small pieces placed near the sides of the vessel being occasionally taken out for judging of the effect of the operation. The second method, which he says is that most generally practiced, is to digest and boil the amber about twenty hours with rapeseed oil, by which it is rendered both clear and hard.

The chemical properties and mode of occurrence of amber leave no doubt of its being the produce of extinct coniferæ. It has been found encrusting or penetrating fossil wood exactly like resin at the present day, and enclosing the cones and leaves of the trees. Numerous insects, the inhabitants of these ancient forests have been embalmed in it. To the tree which principally produced it, Göppert gives the name of *Pinites succinifer*, but there was probably more than one species. Amber is often stated to occur in the brown coal beds of Northern Germany, but Göppert states that he knows of no instance of this, the substance found in those beds being retinite. (Handw. d. Chem. 2te Aufl. ii. 972; Dana, ii. 466; Gerh. iv. 394).

AMBERGRIS. (*Ambra, Ambra grisca*), is found in the sea, near the coasts of various tropical countries; and has also been taken out of the intestines of the spermaceti whale (*Physeter macrocephalus*). As it has not been found in any whales but such as are dead or sick, its production is generally supposed to be owing to disease, though some have a little too positively affirmed it to be the cause of the morbid affection. As no large piece has ever been found without a greater or smaller quantity of the beaks of the *sepio octopodia*, the common food of the spermaceti whale, interspersed throughout its substance, there can be little doubt of its originating in the intestines of the whale: for if it were merely occasionally swallowed by the animal, and then caused disease, it would much more frequently be without these bodies, when it is met with floating in the sea, or thrown upon the shore.

Ambergris is found of various sizes, generally in small fragments, but sometimes so large as to weigh near two hundred pounds. When taken from the whale, it is not so hard as it afterwards becomes on exposure to the air. Its specific gravity ranges from 0·780 to 0·926. If good, it adheres like wax to the edge of a knife with which it is scraped, retains the impression of the teeth or nails, and emits a fat odoriferous liquid on being penetrated with a hot needle. It is generally brittle; but, on rubbing it with the nail, it becomes smooth, like hard soap. Its colour is either white, black, ash-coloured, yellow, or blackish; or it is variegated, namely, grey with black specks, or grey with yellow specks. Its smell is peculiar, and not easy to be counterfeited. At 62·2 C. it melts, and at 100 C. is volatilised in the form of a white vapour; on a red-hot coal it burns, and is entirely dissipated. Water has no action on it; acids, except nitric acid, act feebly on it; alkalis combine with it, and form a soap; ether and the volatile oils dissolve it; so do the fixed oils, and also ammonia, when assisted by heat; alcohol dissolves a portion of it.

The principal constituent of ambergris is ambrein (*q. v.*) Succinic and benzoic acids are said to be sometimes found among the products of its destructive distillation. Its inorganic constituents are carbonate and phosphate of calcium, with traces of ferric oxide and alkaline chlorides.

An alcoholic solution of ambergris, added in minute quantity to lavender water, tooth powder, hair powder, wash balls, &c. communicates its peculiar fragrance. Its retail price being in London a guinea per oz. leads to many adulterations. These consist of various mixtures of benzoin, labdanum, meal, &c. scented with musk. The greasy appearance and smell which heated ambergris exhibits, afford good *criteria*, joined to its solubility in hot ether and alcohol.

It has occasionally been employed in medicine, but its use is now confined to the perfumer. Swediaur took thirty grains of it without perceiving any sensible effect. — U.

AMBLYGONITE. A greenish-coloured mineral of different pale shades, marked on the surface with reddish and yellowish-brown spots. It occurs massive and crystallised in oblique four-sided prisms. Lustre vitreous; cleavage parallel to the sides of an oblique four-sided prism of 106° 10′ and 77° 50′; fracture uneven; fragments rhomboidal; translucent; hardness as felspar; brittle; specific gravity 3·0: intumesces with the blowpipe, and fuses with a reddish-yellow phosphorescence into a white enamel. It occurs in granite, with green topaz and tourmaline, at Chursdorf and Arnsdorf, near Pinig, in Saxony. A specimen from Arsndorf analysed by Rammelsberg gave 47·15 phosphoric anhydride, 88·43 alumina, 7·03 lithia, 3·29 soda, 0·43 potash and 8·11 fluorine, agreeing very nearly with the formula:

$$(5Al^4O^3.3P^2O^5 + 5M^2O.3P^2O^5) + 2\,(Al^2F^3 + MF.)$$

(Handwört. d. Chem. 2te Aufl. i. 665; Dana, ii. 409.)

AMBREIN. By digesting ambergris in hot alcohol, specific gravity 0·827, the peculiar substance, called *ambrein* by Pelletier and Caventou, is obtained. The alcohol, on cooling, deposits the ambrein in very bulky and irregular crystals which still retain a very considerable portion of alcohol. Thus obtained, it has the following properties: — It is of a brilliant white colour, has an agreeable odour, of which it is deprived by repeated solution and crystallisation. It is destitute of taste, and does not act on vegetable blues. It is insoluble in water, but dissolves readily in alcohol and ether; and in much greater quantity in these liquids when hot than when cold. It melts at 30° C. (86° F.) softening at 25° C. When heated above 100° C., it is partly volatilised and decomposed, giving off a white smoke. It does not seem capable of combining with an alkali, or of being saponified. When heated with nitric acid, it becomes green and then yellow, eliminates nitrous gas, and is converted into an acid, which has been called *ambreic* acid. This acid is yellowish white, has a peculiar odour, reddens vegetable blues, does not melt at 100° C., and does not evolve ammonia when decomposed at higher temperatures. It is soluble in alcohol and ether; but slightly so in water. Ambreate of potassium forms yellow precipitates with chloride of calcium, protosulphate of iron, nitrate of silver, acetate of lead, corrosive sublimate, protochloride of tin and chloride of gold. (J. Pharm. v. 49.)

Ambrein is perhaps impure cholesterin, which substance it greatly resembles in its properties. Pelletier (Ann. Ch. Pharm. vi. 24) found it to contain 83·3 p. c. C, 13·3 H, and 3·32 O, which is nearly the composition of cholesterin: if this be so, ambreic acid is probably identical with cholesteric acid.

AMETHANES. A name applied to the ethers of the amic acids, *e. g.* oxamethane to oxamate of ethyl. (See AMIC ACIDS.)

AMETHYST. The amethyst is a gem of a violet colour, and great brilliancy, said to be as hard as the ruby or sapphire, from which it differs only in colour. This is called the oriental amethyst, and is very rare. When it inclines to the purple or rose colour, it is more esteemed than when it is nearer to the blue. These amethysts have the same figure, hardness, specific gravity, and other qualities, as the best sapphires or rubies, and come from the same places, particularly from Persia, Arabia, Armenia, and the West Indies. The occidental amethysts are merely coloured crystals of quartz. — U. (See QUARTZ and SAPPHIRE.)

AMIANTHOID. A variety of Hornblende (*q. v.*)

AMIANTHUS. Mountain flax. (See ASBESTOS.)

AMIC ACIDS. By this name are designated a class of nitrogenised acids, which differ from the acid ammonium-salts of polybasic acids by the elements of one or more atoms of water; and which, under certain circumstances, are capable of taking up the elements of water, and regenerating ammonia and the original non-nitrogenised polybasic acid. They bear a considerable resemblance to amides in their modes both of formation and of decomposition: but they differ from these bodies in possessing invariable and decided acid properties, and in not deriving from the type NH^3.

With regard to their constitution, amic acids are best regarded as deriving from the double type NH^3,H^2O. They represent this type in which 2, 3, or 4 atoms of hydrogen are replaced by other radicles, one of which must be the radicle of a *polybasic* acid: and they may be divided into 3 classes, according as 2, 3, or 4 atoms of hydrogen are so replaced. In class 1, therefore, it is obvious that 2 atoms of hydrogen in the type must be replaced by 1 diatomic acid radicle; in class 2, three atoms of hydrogen may be replaced by 1 triatomic, or by 1 diatomic and 1 monatomic acid radicle; and so on. No amic acid is formed by the substitution of an acid radicle of less than 2 atoms of hydrogen in the type: if 1 atom of hydrogen in NH^3,H^2O be replaced by the radicle of a monobasic acid, the only result is the formation of the ammonium-salt of that acid, *e. g.*:

$$\underset{\text{Acetyl.}}{NH^2(C^2H^3O)HO} = \underset{\text{Acetate of ammonium}}{C^2H^3O.NH^4.O}$$

Neither can an amic acid be formed by replacing 2 atoms hydrogen in the type by 2 monatomic acid radicles; for when benzoic anhydride is treated with ammonia, the 2 atoms of benzoyl, each equivalent to H, do not remain combined, forming an amic acid, but separate, forming 2 distinct compounds, benzamide and benzoate of ammonium:

$$\underset{\text{Benzoic anhyd.}}{(C^7H^5O)^2.O} + 2NH^3 = \underset{\text{Benzamide.}}{N.C^7H^5O.H^2} + \underset{\text{Benzoate of amm.}}{C^7H^5O.NH^4.O}$$

But when a dibasic anhydride is treated with ammonia, the acid radicle, equivalent to H^2, being indivisible, is incapable of separating so as to form two distinct compounds; so that a single compound is necessarily formed, the ammonium-salt of an amic acid:

$$\underset{\text{Sulphuric anhyd.}}{SO^2.O} + 2NH^3 = \underset{\text{Sulphamate of amm.}}{N\overbrace{H^2.S}^{'''}\overbrace{O^2.H}^{''}.O}$$

Hence it follows that a monobasic acid is incapable of forming an amic acid: in fact the possession of this property is perhaps one of the most distinguishing characteristics of polybasic acids.

We now proceed to describe the modes of formation, properties, and reactions of amic acids, dividing them into 3 classes, according as 2, 3, or 4 atoms of hydrogen are replaced in the type.

Class 1. They represent the type $\overbrace{NHHH}^{'''}\ \overbrace{HHO}^{''}$ in which 2 atoms of hydrogen are replaced by one diatomic acid radicle:

Sulphamic acid	$\overbrace{NH.H.S}^{'''}\overbrace{O^2.H}^{''}.O$
Carbamic acid	$\overbrace{NH.H.C}^{'''}\overbrace{O.H}^{''}.O$
Oxamic acid	$\overbrace{NH.H.C^2}^{'''}\overbrace{O^2.H}^{''}.O$
Succinamic acid	$\overbrace{NH.H.C^4}^{'''}\overbrace{H^4O^2.H}^{''}.O$

They are formed—1. By action of heat on the acid ammonium-salt of a dibasic acid:

$$\underset{\text{Acid oxalate of amm.}}{C^2O^2.(NH^4)H.O^2} - H^2O = \underset{\text{Oxamic acid.}}{N.\overbrace{H^2.C^2}^{'''}\overbrace{O^2.H}^{''}.}$$

In some cases, *e. g.* comenamic acid, $NH^2.C^6H^2O^3.H.O$, prolonged boiling of the ammonium-salt with water is sufficient.

2. By action of ammonia on anhydrides:

$$\underset{\text{Camphoric anhyd.}}{C^{10}H^{14}O^2.O} + NH^3 = \underset{\text{Camphoramic acid.}}{N\overbrace{H^2.C^{10}}^{'''}\overbrace{H^{14}O^2.H}^{''}.O}$$

The best mode is to dissolve the anhydride in absolute alcohol, and to lead dry ammonia into the solution. The reaction takes place with 2 atoms of ammonia, an amate of ammonium being formed.

3. By action of ammonia on acid salts of organic radicles:

$$\underset{\substack{\text{Acid salicylate of methyl.}\\ \text{(Methyl-salicylic acid.)}}}{C^7H^4O.(CH^3)H.O^2} + NH^3 = \underset{\text{Salicylamic acid.}}{N\overbrace{H^2.C^7}^{'''}\overbrace{H^4O.H}^{''}.O} + \underset{\substack{\text{Methylic}\\ \text{alcohol.}}}{CH^3.H.O}$$

4. By action of aqueous ammonia on ethers of dibasic acids. (Gerhardt, Chim. org. iv. p. 668.)

$$C^{10}H^{16}O^2.(C^2H^5)^2.O^2 + NH^3 + H^2O = \underset{\text{Sebamic acid.}}{N\overbrace{H^2.C^{10}}^{'''}\overbrace{H^{16}O^2.H}^{''}.O} + 2\left(\underset{\text{Alcohol.}}{C^2H^5.H.O}\right)$$

5. Imides, boiled with dilute ammonia, take up H^2O, and form amic acids: some alkalamides exhibit the same reaction:

$$\underset{\text{Succinimide.}}{N.C^4H^4O^2.H} + H^2O = \underset{\text{Succinamic acid.}}{N\overbrace{H^2.C^4}^{'''}\overbrace{H^4O^2.H}^{''}.O}$$

$$N.C^4H^4O^2.Ag. + H^2O = N\overbrace{H^2.C^4H^4}^{'''}\overbrace{O^2.Ag}^{''}.O$$

Argento-succinimide. Succinamate of silver.

6. Some primary diamides, boiled with mineral acids or alkalis, take up H^2O, and form amic acids, or amates of ammonium:

$$N^2.C^4H^4O^3.H^4 + H^2O = N\overbrace{H^2.C^4H^4}^{'''}\overbrace{O^3}^{''}.H.O + NH^3$$

Malamide. (Asparagine.) Malamic acid. (Aspartic acid.)

7. Some amic acids are formed by the action of hydrosulphuric acid on nitro-conjugated acids:

$$C^7H^4(NO^2)O.H.O + 3H^2S = N\overbrace{H^2.C^7H^4}^{'''}\overbrace{O.H}^{''}.O + 2H^2O + 3S$$

Nitrobenzoic acid. Oxybenzamic acid.

The acid thus formed is commonly called benzamic acid; an impossible name, as benzoic acid is monobasic. We regard it as the amic acid of oxybenzoic acid, $C^7H^4O.H^2.O^2$, a diatomic acid, although it does not form acid salts. Strecker regards this amic acid as phenylcarbamic acid, $NH.C^6H^5.CO.H.O$.

Class 2. They represent the type $N\overbrace{HHH}^{'''}\ \overbrace{HH}^{''}O$ in which 3 atoms hydrogen of are replaced; (a) by 1 triatomic acid radicle, (b) by 1 diatomic and 1 monatomic acid radicle, (c) by 1 diatomic acid, and 1 monatomic basic radicle.

a. 3H *are replaced by* 1 *triatomic acid radicle:*

Phosphamic acid, $N\overbrace{H.PO}^{'''}\overbrace{.H}^{''}.O$, formed by the action of ammonia on phosphoric anhydride:

$$P^2O^5 + 2NH^3 = 2(N.HPO.H.O) + H^2O.$$

b. 3H *are replaced by* 1 *diatomic and* 1 *monatomic acid-radicle:*

Benzoylsalicylamic acid . . . . $N\overbrace{H.C^7H^5O.C^7H^4}^{'''}\overbrace{O.H}^{''}.O$

Sulphophenyl-succinamic acid . . . $N\overbrace{H.C^6H^5SO^2.C^4H^4}^{'''}\overbrace{O^2.H}^{''}.O.$

Obtained by boiling certain tertiary amides with aqueous ammonia (Gerhardt and Chiozza):

$$N.C^6H^5SO^2.C^4H^4O^2 + NH^4.H.O = N\overbrace{H.C^6H^5SO^2.C^4H^4}^{'''}\overbrace{O^2.NH^4}^{''}.O.$$

Sulphophenyl-succinamide. Sulphophenyl-succinamate of amm.

c. 3H *are replaced by* 1 *basic monatomic and* 1 *acid diatomic radicle:*

Ethyloxamic acid . . . . $N\overbrace{H.C^2H^5.C^2}^{'''}\overbrace{O^2.H}^{''}.O$

Phenylsulphamic (sulphanilic) acid . . . $N\overbrace{H.C^6H^5.}^{'''}\overbrace{SO^2.H}^{''}.O$

Phenylsuccinamic (succinanilic) acid . . . $N\overbrace{H.C^6H^5.C^4}^{'''}\overbrace{H^4O^2.H}^{''}.O.$

These compounds (which may be called *alkalamic* acids) are obtained by the same reactions that serve for the formation of acids of class 1, a primary amine being substituted for ammonia:

1. By heating the acid salts of organic alkalis:

$$\overset{''}{C^2}O^2.N(CH^3)H^4.O^2 - H^2O = N\overbrace{H.CH^3.C^2}^{'''}\overbrace{O^2.H}^{''}.O.$$

Acid oxalate of methylium. Methyloxamic acid.

2. By action of primary amines on dibasic anhydrides:

$$C^5\overset{''}{H^6}O^2.O + N.C^6H^5.H^2 = N\overbrace{H.C^6H^5.C^5H^6}^{'''}\overbrace{O^2.H}^{''}.O.$$

Pyrotartaric anhyd. Phenylamine. Phenylpyrotartramic acid.

3. By heating alkalimides with dilute ammonia:

$$\underset{\text{Phenylmalamide.}}{N.C^6H^5.C^4\overset{''}{H}^4O^2} + H^2O = \underset{\text{Phenylmalamic acid.}}{N\overbrace{H.C^6H^5.C^4H^4}^{'''}\overbrace{O^2.H}^{''}.O}.$$

Class 3. They represent the type NH^3,H^2O in which four atoms of hydrogen are replaced by other radicles, one of which must be a polyatomic acid radicle. The only known members of this class are a few phenyl-compounds: phenylcitramic acid, $N.\overbrace{C^6H^5.C^6H^5}^{'''}\overbrace{O^4.H}^{''}.O$, is an example.

There are also certain nitrogenised acids, which either exist ready formed in nature, or are products of the decomposition of other compounds, which we may regard as amic acids. Thus glycocoll, $C^2H^5NO^2$, is the amic acid of glycollic acid, $C^2H^2O.H^2.O^2$, and may be written $NH^2.C^2H^2O.H.O$. Hippuric, choleic, and other acids may also be regarded as amic acids; but their constitution is as yet but imperfectly understood.

Amic acids are distinct monobasic acids: they form well defined salts, which are generally more soluble than those of the corresponding dibasic acids. They are mostly solid, crystalline, not volatile without decomposition. When heated, many of them lose the elements of 1 atom of water, and are converted into imides: others are decomposed into a dibasic anhydride and a primary amine. When boiled with mineral acids or alkalis, they mostly take up the elements of 1 atom of water, and regenerate the corresponding dibasic acid, and ammonia or a primary amine: in some cases, the mere boiling of their aqueous solutions suffices for this reaction; in others, fusion with solid potash is required:

$$\underset{\text{Phenylsuccinamic acid.}}{N\overbrace{H.C^6H^5.C^4H^4}^{'''}\overbrace{O^2.H}^{''}.O} + H^2O = \underset{\text{Succinic acid.}}{C^4\overset{''}{H}^4O^2.H^2.O^2} + \underset{\text{Phenylamine.}}{N.C^6H^5.H^2}$$

With nitrous acid, many amic acids regenerate the corresponding dibasic acid, with evolution of nitrogen:

$$\underset{\text{Malamic acid.}}{\overbrace{NH^2.C^4H^4}^{'''}\overbrace{O^3.H}^{''}.O} + NHO^2 = \underset{\text{Malic acid.}}{C^4\overset{''}{H}^4O^3.H^2.O^2} + N^2 + H^2O.$$

Like all decided acids, amic acids form ethers, *i. e.* salts of alcohol-radicles. These amic ethers are sometimes called *urethanes* (or amethanes), the former name having been applied to the earliest discovered, carbamic ether. They are formed by the incomplete action of ammonia on the ethers of dibasic acids:

$$\underset{\text{Oxalic ether.}}{C^2O^2.(C^2H^5)^2.O^2} + NH^3 = \underset{\text{Oxamic ether.}}{\overbrace{NH^2.C^2}^{'''}\overbrace{O^2.C^2H^5}^{''}.O} + \underset{\text{Alcohol.}}{C^2H^6.H.O}.$$

They are isomeric with alkalamic acids. When boiled with water, acids, or alkalis, they are converted into dibasic acids, alcohol, and ammonia:

$$\underset{\text{Oxamic ether.}}{NH^2.C^2O^2.C^2H^5.O} + 2H^2O = \underset{\text{Oxalic acid.}}{C^2O^2.H^2.O^2} + \underset{\text{Alcohol.}}{C^2H^5.H.O} + NH^3.$$

Excess of ammonia converts them into primary diamides (*q. v.*) — F. T. C.

Amic Bases. This name may be given to a class of bodies produced by the action of ammonia on the oxides, or chloro- or bromo- hydrates of polyatomic alcohol-radicles, and which are related to the polyatomic alcohols in the same way as the *amic acids* to the polyatomic acids. Their leading properties may be expressed by representing them as derived from a combination of the types NH^3 and H^2O.

The following bodies belonging to this class are already known:

$$\text{Anisamine, } C^8H^{11}NO = \left.\begin{matrix}(C^8\overset{''}{H}^8)\\H^3\end{matrix}\right\}\begin{matrix}N\\O\end{matrix};\ \text{type}\left\{\begin{matrix}H^3N\\H^2O\end{matrix}\right.$$

$$\left.\begin{array}{ll}
\text{Dianisamine, } C^{16}H^{19}NO^2 = & \left.\begin{matrix}(C^8\overset{''}{H}^8)^2\\H^3\end{matrix}\right\}\begin{matrix}N\\O^2\end{matrix}\\
\text{Diglycolamine, } C^4H^{11}NO^2 = & \left.\begin{matrix}(C^2\overset{''}{H}^4)^2\\H^3\end{matrix}\right\}\begin{matrix}N\\O^2\end{matrix}\\
\text{Glyceramine, } C^3H^9NO^2 = & \left.\begin{matrix}(C^3\overset{'''}{H}^5)\\H^4\end{matrix}\right\}\begin{matrix}N\\O^2\end{matrix}\\
\text{Diglyceramine, } C^6H^{11}NO^2 = & \left.\begin{matrix}(C^3\overset{'''}{H}^5)^2\\H\end{matrix}\right\}\begin{matrix}N\\O^2\end{matrix}
\end{array}\right\};\ \text{type}\left.\begin{matrix}H^3N\\2(H^2O)\end{matrix}\right\}$$

$$\text{Triglycolamine, } C^6H^{15}NO^3 = \left.\begin{matrix}(C^2\overset{''}{H}^4)^3\\H^3\end{matrix}\right\}\begin{matrix}N\\O^3\end{matrix};\ \text{type}\left.\begin{matrix}H^3N\\3(H^2O)\end{matrix}\right\}$$

AMIDES. Ammonia, NHHH, is capable, under certain circumstances, of exchanging each atom of its hydrogen successively for a metal, or for a compound radicle, acid or basic, — thus giving rise to a numerous class of compounds, all deriving from the same type, NHHH. The earliest discovered of these compounds were some of those in which *one* atom of hydrogen was thus replaced, *e. g.* NHHK, which was regarded as a compound of NH^2 (*amidogen*) with potassium, NH^2K, and called *amide* of potassium, analogous to the cyanide, CNK. In process of time, compounds came to be discovered, deriving from the type NHHH, in which 2 or 3 atoms of hydrogen were replaced by metals or compound radicles, to which the name amide in its original sense of a compound containing amidogen, NH^2, was plainly inapplicable; accordingly these compounds were designated by other names, *imides*, *nitriles*, &c., the introduction of which has caused considerable confusion, since they in no way indicate the common derivation of all these compounds.

Of late years attempts have been made, chiefly by Gerhardt, to remedy this confusion, by assigning to this numerous class of compounds a rational constitution which shall render evident their common derivation, and a nomenclature by which this constitution is at once expressed. These attempts have been attended with considerable success: and the classification adopted in this article is based upon that given by Gerhardt and Chiozza (Ann. Ch. Phys. [3] xlvi.), certain modifications being introduced where greater clearness seems thereby to be attained.

Since the hydrogen in ammonia is capable of being replaced either by acid- or by base-radicles (simple or compound), the first obvious division of the compounds thus formed is one based upon the *nature* of the radicle which has been substituted for hydrogen. These compounds thus fall into three great divisions:

1. Ammonias in which 1 or more atoms of hydrogen are replaced by an *acid*-radicle. To this division we propose to confine the name of amides. In the case of each individual member of the class, the generic name is preceded by a prefix, which indicates the particular acid radicle or radicles contained in the compound, *e. g.* acetamide $N.C^2H^3O.H^2$, diacetamide $N.(C^2H^3O)^2H$, &c.

2. Ammonias in which 1 or more atoms of hydrogen are replaced by *base*-radicles. This division we call amines. For examples of the nomenclature of individuals, we may take potassamine, $N.K.H^2$, ethylamine, $N.C^2H^5.H^2$, methylethylamine, $N.CH^3.C^2H^5.H$, &c.

3. Ammonias in which 2 or more atoms of hydrogen are replaced by *acid*- and *base*-radicles. This division we call alkalamides. Examples are ethylacetamide, $N.C^2H^5.C^2H^3O.H$, phenyldibenzamide, $N.C^6H^5.(C^7H^5O)^2$.

This primary classification enables us to perceive in compounds deriving from the type ammonia, NHHH, the same seriation of properties which was first pointed out by Gerhardt in the compounds deriving from the type oxide, OHH. As in the latter case, we have metallic oxides (bases) occupying the positive extreme, acids the negative extreme, while the middle place is filled up by salts, containing at once an acid- and a base-radicle; so in the former case, we have amines at the positive extreme, amides at the negative, and alkalamides between the two extremes.

A further ground for division is furnished by the fact that amides, amines, and alkalamides may derive from 1, 2, or 3 molecules of ammonia, according as they contain monatomic, diatomic, or triatomic radicles. Hence we have a further division of amides into

1. *Monamides* (or amides), deriving from 1 mol. ammonia NHHH.
2. *Diamides* „ „ 2 mols. „ $N^2H^2H^2H^2$.
3. *Triamides* „ „ 3 mols. „ $N^3H^3H^3H^3$.

The same subdivision applies to amines and alkalamides.

In each of these types, NHHH, $N^2H^2H^2H^2$, $N^3H^3H^3H^3$, one third, two thirds, or the whole of the hydrogen may be replaced by acid- or base-radicles: hence arises a further division of amides, diamides, and triamides into:

1. *Primary*, in wh. $\frac{1}{3}$ of the hydrogen is replaced, NAHH, $N^2A''H^2H^2$, $N^3A'''H^3H^3$.
2. *Secondary*, in wh. $\frac{2}{3}$ of the hydrogen is replaced, NA^2H, $N^2(A'')^2H^2$, $N^3(A''')^2H^3$.
3. *Tertiary*, in wh. the whole of the hydrogen is replaced, NA^3, $N^2(A'')^3$, $N^3(A''')^3$.

The same subdivision applies to amines, and (partially) to alkalamides.

Having thus indicated the general principles of classification which we adopt, we now proceed to the more detailed consideration of amides, amines, and alkalamides. It is not our purpose to give a complete list of these compounds, but merely to cite a sufficient number of them to illustrate our classification; and to enumerate the principal reactions by which the formation and decomposition of each group is effected.

AMIDES.

I. Monamides or Amides.

1. *Primary Amides.* They represent 1 molecule of ammonia, in which 1 atom of hydrogen is replaced by a monatomic acid-radicle (of a monobasic acid):

Acetamide	$N.C^2H^3O.H^2$
Propionamide	$N.C^3H^5O.H^2$
Benzamide	$N.C^7H^5O.H^2$
Cyanamide	$N.CN.H^2$
Sulphophenylamide	$N.C^6H^5SO^2.H^2$.

They differ from the ammonium-salt of their acids in containing the element of 1 atom of water less:

$$\underset{\text{Acet. amm.}}{C^2H^3O^2(NH^4)} - H^2O = \underset{\text{Acetamide.}}{N.C^2H^3O.H^2}$$

They are formed: 1. By the action of ammonia on anhydrides (Gerhardt).

$$\underset{\text{Benzoic anhyd.}}{(C^7H^5O)^2O} + NH^3 = \underset{\text{Benzoic acid.}}{C^7H^5O.H.O} + \underset{\text{Benzamide.}}{N.C^7H^5O.H^2}$$

2. By the action of ammonia (Liebig and Wöhler), or of carbonate of ammonium (Gerhardt) on the chlorides of acid-radicles:

$$\underset{\substack{\text{Chloride of}\\ \text{cyanogen.}}}{CNCl} + NH^3 = HCl + \underset{\text{Cyanamide.}}{N.CN.H^2}$$

This method is especially adapted to the formation of those amides which are insoluble or nearly so, in water.

3. By the action of ammonia on ethers:

$$\underset{\text{Acetic ether.}}{C^2H^3O.C^2H^5.O} + NH^3 = \underset{\text{Alcohol.}}{C^2H^6O} + \underset{\text{Acetamide.}}{N.C^2H^3O.H^2}$$

This method is peculiarly adapted to the formation of soluble amides. Glycerides, with ammonia, also yield an amide, and glycerin. (Berthelot.)

4. Some primary amides have special methods of formation: *e. g.* benzamide is formed by oxidising hippuric acid with peroxide of lead:

$$C^9H^9NO^3 + 3O = N.C^7H^5O.H^2 + 2CO^2 + H^2O$$

Primary amides are mostly solid and crystalline, easily fusible, neutral to test paper, volatile without decomposition. Some of them, *e. g.* acetamide, combine with acids: others *e. g.* benzamide, can exchange 1 atom of hydrogen for a metal, forming metallic salts, or alkalamides. They are generally soluble in alcohol or ether: some in water.

Reactions.—1. Boiled with acids or with alkalis (some with water), they take up H^2O and regenerate the acid and ammonia.

2. Treated with phosphoric anhydride, they lose H^2O, and yield the corresponding nitrile. The same reaction frequently takes place when they are passed in the state of vapour over caustic lime.

$$\underset{\text{Acetamide.}}{N.C^2H^3O.H^2} - H^2O = \underset{\substack{\text{Aceto-}\\ \text{nitrile.}}}{N.C^2H^3}$$

3. Treated with pentachloride of phosphorus, they behave as though they were oxides, yielding oxychloride of phosphorus, and the chloride of the radicle which they may be supposed to contain, if derived from the type HHO (Gerhardt):

$$\underset{\text{Benzamide.}}{C^7H^6N.H.O} + PCl^5 = PCl^3O + HCl + \underset{\substack{\text{Chloride of}\\ \text{benzamyl.}}}{C^7H^6N.Cl}$$

The chloride thus formed is readily decomposed by heat, frequently below 100° C. into hydrochloric acid and the corresponding nitrile, $C^2H^4NCl = HCl + N.C^2H^3$ (aceto-nitrile).

4. With nitrous acid they yield their corresponding acid, with evolution of nitrogen:

$$\underset{\text{Benzamide.}}{N.C^7H^5O.H^2} + NO^2H = NN + H^2O + \underset{\substack{\text{Benzoic}\\ \text{acid.}}}{C^7H^6O^2}$$

2. *Secondary Amides.*—They represent 1 molecule of ammonia, in which 2 atoms of hydrogen are replaced: (*a*) by 2 monatomic acid-radicles. (*b*) by 1 diatomic acid-radicle of a (dibasic acid).

a. $\mathrm{H^2}$ *are replaced by* 2 *monatomic radicles:*

Diacetamide	$\mathrm{N.(C^2H^3O)^2.H}$
Sulphophenyl-benzamide	$\mathrm{N.C^6H^5SO^2.C^7H^5O.H}$

They are formed: 1. By the action of chlorides of acid-radicles on primary amides, or their metallic salts (Gerhardt):

$$\mathrm{N.C^6H^5SO^2.H^2 + C^7H^5O.Cl = HCl + N.C^6H^5SO^2.C^7H^5O.H.}$$

Sulphophenylamide — Chloride of benzoyl. — Sulphophenyl-benzamide.

2. By action of dry hydrochloric acid on primary amides, at a high temperature (Strecker):

$$\mathrm{2(N.C^2H^3O.H^2) + HCl = NH^4Cl + N.(C^2H^3O)^2.H}$$

Acetamide. — Diacetamide.

These amides are readily soluble in ammonia. They exhibit acid properties, reddening litmus, and exchanging their remaining atom of hydrogen for a metal: the metallic salts thus formed dissolve in ammonia, producing compounds which Gerhardt regards as dialkalamides, but which, as they contain only monatomic radicles, it is perhaps preferable to regard as monalkalamides containing a compound ammonium:

$$\mathrm{N.C^6H^5SO^2.C^7H^5O.Ag. + NH^3 = N.C^6H^5SO^2.C^7H^5O.NAgH^3}\ \text{(monalkalamide).}$$
$$\text{or } \mathrm{N^2.C^6H^5SO^2.C^7H^5O.Ag.H^3}\ \text{(dialkalamide).}$$

According to Gerhardt (Ann. Ch. Phys. [3] liii.); pentachloride of phosphorus acts on secondary amides in the same way as on primary amides:

$$\mathrm{N.C^6H^5SO^2.C^7H^5O.H + PCl^5 = PCl^3O + HCl + N(C^7H^5)(C^6H^5SO^2)Cl}$$

Sulphophenylbenzamide. — Chloride of sulphophenyl-bexamidyl.

and the chloride formed is decomposed by heat:

$$\mathrm{N(C^7H^5)(C^6H^5SO^2)Cl = N.C^7H^5 + C^6HSO^2.Cl}$$

Benzonitrile. — Chloride of sulphophenyl.

b. $\mathrm{H^2}$ *are replaced by* 1 *diatomic radicle.* These are the bodies generally called *imides*, being regarded as containing *imidogen*, NH. Though we reject this view of their constitution, we retain the name for convenience sake.

Carbimide (cyanic acid)	$\mathrm{N.(CO)''.H}$
Succinimide	$\mathrm{N.(C^4H^4O^2)''.H}$
Camphorimide	$\mathrm{N.(C^{10}H^{14}O^2)''.H.}$

They differ from the acid ammonium-salts of their acids by containing 2 atoms of water less:

$$\mathrm{C^4H^4O^4(NH^4)H - 2H^2O = N.C^4H^4O^2.H}$$

Acid succinate of ammonium. — Succinimide.

They are formed much more easily than secondary amides (*a*):

1. By heating the acid ammonium-salts of dibasic acids.
2. By heating primary diamides:

$$\mathrm{N^2.C^4H^4O^2.H^4 = N.C^4H^4O^2.H + NH^3.}$$

Succinamide. — Succinimide.

3. By heating amic acids (Laurent):

$$\mathrm{N.C^{10}H^{14}O^2.H^2.H.O = H^2O + N.C^{10}H^{14}O^2.H}$$

Camphoramic acid. — Camphorimide.

4. By heating dibasic anhydrides with ammonia:

$$\mathrm{C^4H^4O^2.O + NH^3 = H^2O + N.C^4H^4O^2.H}$$

Succinic anhydride. — Succinimide.

Imides possess decided acid properties, and readily exchange their basic hydrogen for a metal; carbimide in fact is identical with cyanic acid.

Reactions.—1. Boiled with acids or alkalis, they take up $\mathrm{2H^2O}$ and regenerate the dibasic acid and ammonia:

$$\mathrm{N.C^4H^4O^2.H + 2H^2O = C^4H^4O^4.H^2 + NH^3.}$$

Secondary amides (*a*) also exhibit this reaction.

2. Boiled with dilute ammonia, they form the ammonium-salt of the corresponding amic acid:

$$\mathrm{N.C^4H^4O^2.H + NH^4.HO = N.C^4H^4O^2.H^2.NH^4.O}$$

Succinamate of amm.

3. *Tertiary Amides.*—They represent 1 molecule of ammonia, in which all the hydrogen is replaced: (*a*) by 3 monatomic, (*b*) by 1 diatomic and 1 monatomic, (*c*) by 1 triatomic, acid-radicle:

a. H^3 *are replaced by* 3 *monatomic radicles:*

Sulphophenyl-benzoyl-acetamide . . $N.C^6H^5SO^2.C^7H^5O.C^2H^3O$.

b. H^3 *are replaced by* 1 *diatomic and* 1 *monatomic radicle:*

Sulphophenyl-succinamide . . . $N.C^6H^5SO^2.(C^4H^4O^2)''$.

They are formed by the action of chlorides of acid-radicles on the metallic salts of secondary amides (tertiary alkalamides):

$$N.C^6H^5SO^2.C^7H^5O.Ag + C^2H^3O.Cl = AgCl + N.C^6H^5SO^2.C^7H^5O.C^2H^3O$$
$$N.C^4H^4O^2.Ag + C^6H^5SO^2.Cl = AgCl + N.C^4H^4O^2.C^6H^5SO^2.$$

Their reactions are but little known. Boiled with dilute ammonia, the amides of class (*b*) give the ammonium-salt of the corresponding amic acid:

$$\underset{\text{Sulphophenyl-succinamide.}}{N.C^4H^4O^2.C^6H^5SO^2} + NH^4.H.O = \underset{\text{Sulphophenyl-succinamate of ammonium.}}{NC^4H^4O^2.C^6H^5SO^2.H.NH^4.O.}$$

c. H^3 *are replaced by* 1 *triatomic radicle.* To this group, by their reactions and mode of formation, the following mineral compounds belong:

$N.(PO)'''$.	Gerhardt's biphosphamide	(phosphorylamide)	$= PO^4(NH^4)H^2 - 3H^2O$
$N.N.'''$.	Free nitrogen	(Nitroso-nitrile)	$= NO^2.NH^4 - 2H^2O$
$N.(NO)'''$.	Nitrous oxide.	(Nitro-nitrile)	$= NO^3.NH^4 - 2H^2O.$

II. **Diamides.**

1. *Primary Diamides.*—They represent 2 molecules of ammonia in which 2 atoms of hydrogen are replaced by 1 diatomic acid-radicle.

Sulphamide	$N^2.(SO^2)''.H^4$
Oxamide	$N^2.(C^2O^2)''.H^4$
Succinamide	$N^2.(C^4H^4O^2)''.H^4$
Carbamide (urea)	$N^2.(CO)''.H^4$

They differ from the normal ammonium-salts of their acids in containing 2 atoms of water less:

$$\underset{\text{Oxalate of ammonium.}}{C^2O^4(NH^4)^2} - 2H^2O = \underset{\text{Oxamide.}}{N^2.C^2O^2.H^4}$$

They are formed—1. By the action of ammonia on ethers:

$$\underset{\text{Oxalic ether.}}{C^2O^4(C^2H^5)^2} + 2NH^3 = 2C^2H^6O + \underset{\text{Oxamide.}}{N^2.C^2O^2.H^4}$$

2. By the action of ammonia on chlorides of acid-radicles:

$$\underset{\text{Chloride of succinyl.}}{C^4H^4O^2.Cl^2} + 2NH^3 = 2HCl + \underset{\text{Succinamide.}}{N^2.C^4H^4O^2.H^4}$$

3. By heating normal ammonium-salts of dibasic acids (Dumas).
4. By the action of ammonia on imides (Wöhler):

$$\underset{\text{Carbimide.}}{N.CO.H} + NH^3 = \underset{\text{Carbamide.}}{N^2.CO.H^4}$$

By the action of ammonia on dibasic anhydrides, not primary diamides, but amic acids, are generally formed.

Many primary diamides exhibit decidedly basic properties, combining with acids and forming definite salts: *e.g.* urea, asparagine, &c.

Reactions.—1. Many of them, when heated, evolve ammonia and yield imides. 2. Boiled with acids or alkalis, they take up $2H^2O$, and regenerate the acid and ammonia:

$$N^2.C^2O^2.H^4 + 2H^2O = C^2O^4.H^2 + 2NH^3.$$

3. With nitrous acid, they regenerate their dibasic acid, with evolution of nitrogen (Piria, Malaguti):

$$\underset{\text{Oxamide.}}{N^2.C^2O^2.H^4} + 2NO^2H = 2NN + \underset{\text{Oxalic acid.}}{C^2O^4.H^2} + 2H^2O.$$

Intermediate between primary and secondary diamides must be classed the bodies lately discovered by Zinin (Ann. Ch. Phys. [3] xliv. 57), which he describes as ureas, in which 1 atom of hydrogen is replaced by an acid radicle. They are of course diamides, in which 3 atoms of hydrogen are replaced, 2 by a diatomic, and 1 by a monatomic radicle.

Acetocarbamide (acetyl-urea) . .	$N^2.CO.C^2H^3O.H^3$
Benzocarbamide (benzoyl-urea) . .	$N^2.CO.C^7H^5O.H^3$.

They are formed by the action of chlorides of acid-radicles on urea:

$$\underset{\text{Carbamide.}}{N^2.CO.H^4} + \underset{\text{Chloride of acetyl.}}{C^2H^3O.Cl} = HCl + \underset{\text{Acetocarbamide.}}{N^2.CO.C^2H^3OH^3}$$

Attempts to replace more than 1 atom of hydrogen in urea by an acid-radicle, have hitherto failed.

These bodies are crystallisable, and do not combine with acids. They are not volatile, being decomposed by heat into cyanuric acid and a primary amide:

$$\underset{\text{Acetocarbamide.}}{3(N^2.CO.C^2H^3O.H^3)} = \underset{\text{Cyanuric acid.}}{C^3N^3O^3H^3} + \underset{\text{Acetamide.}}{3(N.C^2H^3O.H^2)}$$

Here too must be placed Gerhardt's phosphamide (Ann. Ch. Phys. [3] xviii.)—$N^2.(PO)'''.H^3$, formed by saturating pentachloride of phosphorus with ammonia, and boiling with water:

$$PCl^5 + 2NH^3 + H^2O = N^2.PO.H^3 + 5HCl.$$

It differs from monacid phosphate of ammonium by the elements of 3 atoms of water:

$$PO^4(NH^4)^2H - 3H^2O = N^2.PO.H^3.$$

2. *Secondary Diamides.*—They represent 2 molecules of ammonia, in which 4 atoms hydrogen are replaced by 2 diatomic acid-radicles, or by 1 diatomic and 2 monatomic radicles.

None of these have yet been formed. (Handwb.)

3. *Tertiary Diamides.*—They represent 2 molecules of ammonia, in which all the hydrogen is replaced by acid-radicles, one of which at least must be dibasic:

Trisuccinamide	$N^2.(C^4H^4O^2)^3$
Succinyl-disulphophenyl-dibenzamide .	$N^2.(C^4H^4O^2).(C^6H^5SO^2)^2.(C^7H^5O)^2$.

They are formed by the action of chlorides of acid-radicles on the silver-salts of secondary amides:

$$\underset{\text{Argentosuccinamide.}}{2(N.C^4H^4O^2.Ag)} + \underset{\text{Chloride of succinyl.}}{C^4H^4O^2.Cl^2} + \underset{\text{Trisuccinamide.}}{N^2.(C^4H^4O^2)^3} + 2AgCl.$$

III. **Triamides.**

1. *Primary Triamides.*—They represent 3 molecules of ammonia, in which 3 atoms of hydrogen are replaced by a triatomic acid-radicle:

Phosphamide	$N^3.(PO)'''.H^6$.
Citramide	$N^3.(C^6H^5O^4)'''.H^6$.

They differ from the normal ammonium-salts of their acids by containing $3H^2O$ less:

$$\underset{\text{Citrate of amm.}}{C^6H^5O^7(NH^4)^3} - 3H^2O = \underset{\text{Citramide.}}{N^3.C^6H^5O^4.H^6}.$$

Phosphamide is formed by the action of ammonia on oxychloride of phosphorus: $POCl^3 + 6NH^3 = 3NH^4Cl + N^3.PO.H^6$. (Schiff. Ann. Ch. Pharm. ci. 300.)

Citramide is formed by the action of ammonia on citric ether:

$$\underset{\text{Citric ether.}}{C^6H^5O^4.(C^2H^5)^3.O^3} + 3NH^3 = \underset{\text{Citramide.}}{N^3.C^6H^5O^4.H^6} + \underset{\text{Alcohol.}}{3(C^2H^5.H.O)}$$

Heated with acids or alkalis, they take up $3H^2O$, and regenerate their acid and ammonia.

2. *Secondary Triamides.*
3. *Tertiary Triamides.*

They represent respectively 3 mols. ammonia, in which two-thirds and the whole of the hydrogen is replaced by acid-radicles, one of which at least must be triatomic.

No member of either of these groups has yet been formed.

Gerhardt (Chim. org. iv. p. 767) regards melam, $C^3H^6N^6$, as a primary triamide, $N^3.C^3N^3.H^6$: and indeed we may admit the existence of a triatomic radicle, C^3N^3, and regard hydrocyanic acid as tribasic, $C^3N^3H^3$: otherwise such compounds as ferrocyanide of potassium, $C^6N^6FeK^2$, present the anomaly of bodies deriving from a triple type (H^3Cl^3), and yet containing only monatomic radicles.

AMINES.

I. **Monamines** or **Amines.**

1. *Primary Amines.*—They represent 1 molecule of ammonia, in which 1 atom of hydrogen is replaced by a monatomic base-radicle, whether a metal or an organic radicle. They are sometimes called *amide-bases.*

Potassamine	$N.K.H^2$
Platinamine	$N.Pt.H^2$.
Methylamine	$N.CH^3.H^2$
Ethylamine	$N.C^2H^5.H^2$
Phenylamine (Aniline) . . .	$N.C^6H^5.H^2$.

Primary amines containing metals are generally obtained by the action of ammonia on the metal or its oxide. Zincamine is formed by the action of ammonia on zinc-ethyl: $ZnC^2H^5 + NH^3 = H.C^2H^5 + NZnH^2$.—When treated with water or acids, they are mostly decomposed, like primary amides, yielding ammonia and the hydrate of the metal.

Primary amines containing organic radicles are formed:

1. By action of ammonia on hydrobromic or hydriodic ethers (Hofmann):

$$\underset{\text{Iodide of methyl.}}{CH^3I} + NH^3 = HI + \underset{\text{Methylamine.}}{N.CH^3.H^2}$$

2. By action of potash on cyanic or cyanuric ethers (Wurtz):

$$\underset{\text{Cyanate of methyl.}}{N.CO.CH^3} + K^2H^2O^2 = \underset{\text{Carbonate of potassium.}}{CO.K^2.O^2} + \underset{\text{Methyl-amine.}}{N.CH^3.H^2}$$

3. By action of reducing agents, viz. alkaline hydrosulphates (Zinin), acetate of iron (Béchamp), on certain nitro-conjugated hydrocarbons:

$$\underset{\text{Nitrobenzene.}}{C^6H^5(NO^2)} + H^6 = 2H^2O + \underset{\text{Phenylamine.}}{N.C^6H^5.H^2}$$

Their formation is also observed in the dry distillation of several nitrogenised organic substances. (For the various modes of formation of monamines in general, primary, secondary, and tertiary, see Kékulé, Lehrb. d. org. Chemie, pp. 451—456.)

These primary amines are mostly liquid, boiling at a low temperature, and volatile without decomposition. They strikingly resemble ammonia in all their properties: like it they have a strong alkaline reaction; they combine directly with acids, forming salts, whence they are expelled by the fixed alkalis; they precipitate metallic solutions; with anhydrides, ethers, and chlorides of acid-radicles, they react precisely like ammonia (forming alkalamides, *q. v.*), and with hydriodic ethers they form diamides. With nitrous acid they yield nitrous ether or alcohol, with evolution of nitrogen:

$$\underset{\text{Ethylamine.}}{N.C^2H^5.H^2} + 2NO^2H = NN + 2H^2O + \underset{\text{Nitrous ether.}}{NO^2.C^2H^5}$$

$$\underset{\text{Phenylamine.}}{N.C^6H^5.H^2} + NO^2H = NN + H^2O + \underset{\text{Phenylic alcohol.}}{C^6H^6O}$$

In this group must also be included those amines whose radicle contains chlorine, bromine, iodine, or nitryl (NO^2), substituted for 1, 2, or 3 atoms of hydrogen: *e. g.* Dichlorethylamine, $N.C^2H^3Cl^2.H^2$, Chlorophenylamine, $N.C^6H^4Cl.H^2$, Dichlorphenylamine, $N.C^6H^3Cl^2.H^2$, Trichlorphenylamine, $N.C^6H^2Cl^3.H^2$, Nitrophenylamine, $N.C^6H^4.(NO^2).H^2$, &c. Their alkaline properties are less marked, the greater the number of atoms of chlorine, &c. they contain. They are formed mostly either by the direct action of chlorine, &c. on amines, or by the metamorphoses of other conjugated compounds. Nitrophenylamine is formed by the reduction of dinitrobenzene by hydrosulphate of ammonium, just as phenylamine results from the reduction of nitrobenzene by the same agent.

2. *Secondary Amines.*—They correspond to 1 molecule of ammonia, in which 2 atoms of hydrogen are replaced by two monatomic base-radicles. They are sometimes called *Imide-bases.*

Dimethylamine	$N.(CH^3)^2.H$.
Methylethylamine	$N.CH^3.C^2H^5.H$.
Ethylphenylamine	$N.C^2H^5.C^6H^5.H$.

They are formed by the action of hydriodic ethers on primary amines:

$$\underset{\text{Methylamine.}}{N.CH^3.H^2} + \underset{\text{Iodide of ethyl.}}{C^2H^5I} = HI + \underset{\text{Methylethylamine.}}{N.CH^3.C^2H.^5H}$$

In properties and reactions, they closely resemble primary amines: but they are in general less volatile.

We must also regard as secondary amines two alkaloids, which have not yet been formed artificially:

Piperidine	$N.(C^5H^{10})''.H.$
Conine	$N.(C^8H^{14})''.H.$

The chemical relations of the radicles contained in these compounds are as yet unknown to us; and we cannot determine whether they are single diatomic radicles, or whether they are made up of two monatomic radicles.

3. *Tertiary Amines.*—They represent 1 molecule of ammonia, in which all the hydrogen is replaced: (*a*) by 3 monatomic, (*b*) by 1 diatomic and 1 monatomic, (*c*) by 1 triatomic base-radicle.

a. H^3 are replaced by 3 monatomic radicles (Nitrile-bases).

Tripotassamine	$N.K^3$
Trimercuramine	$N.Hg^3$
Trimethylamine	$N.(CH^3)^3$
Methyldiethylamine	$N.CH^3.(C^2H^5)^2.$
Methylethylphenylamine	$N.CH^3.C^2H^5.C^6H^5.$

Those containing organic radicles are formed—1. By the action of hydriodic ethers on secondary amines:

$$\underset{\text{Dimethylamine.}}{N.(CH^3)^2.H} + \underset{\text{Iodide of ethyl.}}{C^2H^5.I} = HI + \underset{\text{Dimethylethylamine.}}{N.(CH^3)^2.C^2H^5.}$$

2. By the distillation of the salts of organic ammonium-bases:

$$\underset{\text{Hydrate of tetrethylium.}}{N.(C^2H^5)^4.H.O} = \underset{\text{Triethylamine.}}{N.(C^2H^5)^3} + \underset{\text{Ethylene.}}{C^2H^4} + H^2O$$

$$\underset{\text{Iodide of tetrethylium.}}{N(C^2H^5)^4.I} = N.(C^2H^5)^3 + C^2H^5I.$$

3. By action of ethylate of potassium on cyanic ether:

$$\underset{\text{Cyanate of ethyl.}}{N.CO.C^2H^5} + \underset{\text{2 mol. ethylate of potassium.}}{(C^2H^5)^2.K^2.O^2} = \underset{\text{Triethylamine.}}{N.(C^2H^5)^3} + \underset{\text{Carbonate of potassium.}}{CO.K^2.O^2}$$

This reaction is analogous to that of hydrate of potassium on cyanic ethers. (See PRIMARY AMINES.)

Tertiary amines are generally similar in properties to primary and secondary amines: they are less volatile than either. They are however distinguished by one important reaction, which at the same time exhibits in the strongest light their analogy with the type from which they are derived. When acted upon by hydriodic ethers, direct combination takes place, an iodide of an organic ammonium-base being formed:

$$N.(C^2H^5)^3 + C^2H^5.I = \underset{\text{Iodide of tetrethylium.}}{N(C^2H^5)^4.I}$$

These iodides are usually crystalline, soluble in water and alcohol: when treated with oxide of silver, they yield iodide of silver, and a hydrate of the ammonium-base:

$$2[N(C^2H^5)^4.I] + Ag^2O + H^2O = 2AgI + 2[\underset{\text{Hydrate of tetrethylium.}}{N(C^2H^5)^4.H.O}]$$

These hydrates are crystalline and soluble in water: they are powerful alkalis; in some reactions they resemble the fixed alkalis, liberating ammonia from ammoniacal salts, and decomposing ethers into acid and alcohol. Precisely, therefore, as ammonia (nitride of hydrogen) NH^3, combines with hydriodic acid (iodide of hydrogen) HI, forming iodide of ammonium, NH^4I; so triethylamine (nitride of ethyl) $N(C^2H^5)^3$, combines with iodide of ethyl, C^2H^5I, forming iodide of tetrethylium, $N(C^2H^5)^4I$. Just as we have the hypothetical compound ammonium, NH^4, playing the part of potassium, sodium, and other metals, and replacing the basic hydrogen in acids to form salts—so we have the hypothetical compound tetrethylium, $N(C^2H^5)$, performing precisely the same metallic functions. The analogy could not be more complete.

b. H^3 are replaced by 1 diatomic and 1 monatomic radicle: Hofmann's ethylenephenylamine, $N.(C^2H^4)''.C^6H^5.$

c. H^3 are replaced by 1 triatomic radicle (Nitriles).

Acetonitrile (cyanide of methyl)	$N.(C^2H^3)'''$
Propionitrile (cyanide of ethyl)	$N.(C^3H^5)'''$
Benzonitrile (cyanide of phenyl)	$N.(C^7H^5)'''$.

They are formed—1. By the action of heat or dehydrating agents (*e.g.* phosphoric anhydride) on ammoniacal salts of monobasic acids:

$$\underset{\text{Acetate of amm.}}{C^2H^3O^2.NH^4} - 2H^2O = \underset{\text{Acetonitrile.}}{N.C^2H^3}.$$

These nitriles differ from primary amides in containing H^2O less.

2. By the action of cyanide of potassium on sulphate of ethyl and potassium (or a homologous salt), or on hydriodic ethers:

$$\underset{\substack{\text{Sulphate of ethyl}\\\text{and potassium.}}}{SO^2.(C^2H^5).K.O^2} + CN.K = \underset{\substack{\text{Sulphate of}\\\text{potassium.}}}{SO^2.K^2.O^2} + \underset{\substack{\text{Cyanide of}\\\text{ethyl or}\\\text{propio-nitrile.}}}{CN.C^2H^5}$$

This mode of formation shows that nitriles may also be regarded as cyanides ($N.C^2H^3 = CN.CH^3$), deriving from the type ClH: and it is in this light that they are usually considered. But, if we consider their formation from ammoniacal salts, and their behaviour when boiled with acids or alkalis, when they regenerate their acid and ammonia,—$NC^2H^3 + KHO + H^2O = C^2H^3O^2K + NH^3$,—we may fairly regard them as deriving from the same type with amides. And we are led to consider them as amines rather than as amides, by the fact that, in one of them at least, the radicle is clearly a basic one; in propio-nitrile, $N.C^3H^5$, the radicle is *glyceryl*, the triatomic radicle of the triatomic alcohol, glycerin, $C^3H^5.H^3.O^3$. Moreover, that they resemble amines in the property of combining with acids, is shown by the compounds which Gerhardt obtained by the action of pentachloride of phosphorus on primary amides (*q. v.*) $C^7H^6NCl = N.C^7H^5 + HCl$.

In order to show the connection between nitriles and the acids from whose ammonium-salts they are formed, *e.g.* of acetonitrile $N.C^2H^3$, with acetic acid, $C^2H^4O^2$, and acetic compounds generally, it may be observed that acetic compounds may be represented as containing the triatomic radicle C^2H^3. Thus acetic acid may be written $(C^2H^3)'''.H.O^2$, deriving from the double type H^4O^2: acetamide, $N.H.C^2H^3.H.O$, deriving from the double type $NH^3 + H^2O$: chloride of acetyl, $Cl.C^2H^3.O$, deriving from the double type $ClH + H^2O$: acediamine, $N^2.C^2H^3.H^3$, deriving from the double type N^2H^6.

We have already seen that, when an amine which contains any replaceable hydrogen (primary or secondary amines), is treated with the iodide of an organic basic radicle, the result is the replacement of the basic hydrogen by the organic radicle: but that when tertiary amines, in which all the basic hydrogen is already replaced, are similarly treated, the result is a direct combination of the iodide with the amine. Hence we are enabled to class as tertiary amines many natural organic alkalis, which combine directly with organic iodides; of whose constitution, as they cannot be formed artificially, we should otherwise be ignorant. Among these are the following homologous alkalis, obtained by the dry distillation of animal matter:

Pyridine	$N.C^5H^5$
Picoline	$N.C^6H^7$
Lutidine	$N.C^7H^9$
Collidine	$N.C^8H^{11}$
Parvoline	$N.C^9H^{13}$.

Also the numerous vegetable alkalis or alkaloids (quinine, strychnine, morphine, &c.), which have been extracted from plants. The majority of these latter compounds contain oxygen-radicles: as many of them contain 2 atoms of nitrogen, it is possible that they must be regarded as diamines. How many radicles they may contain, we have as yet no means of determining.

II. **Diamines.**

1. *Primary Diamines.* } They represent 2 molecules of ammonia, in which
2. *Secondary Diamines.* } 2 and 4 atoms of hydrogen are replaced by 1 and 2 diatomic base-radicles. The only representatives of these groups are the compounds lately obtained by Hofmann, by the action of bromide of ethylene on ammonia; they contain the diatomic radicle ethylene, C^2H^4:

Ethylenamine	$N^2.\overset{\prime\prime}{(C^2H^4)}.H^4$
Diethylenamine	$N^2.\overset{\prime\prime}{(C^2H^4)}{}^2.H^2$.

They are thus formed:

$$\underset{\text{Bromide of ethylene.}}{C^2H^4.Br^2} + N^2H^6 = 2HBr + \underset{\text{Ethylenamine.}}{N^2.\overset{''}{C^2}H^4.H^4}$$

$$2C^2H^4Br^2 + N^2H^6 = 4HBr + \underset{\text{Di-ethylenamine.}}{N^2.(\overset{''}{C^2}H^4)^2.H^2}$$

Intermediate between secondary and tertiary diamines, is Hofmann's diphenylformylamine, $N^2.(C^6H^5)^2.CH.H$, obtained by the action of chloroform on phenylamine; $2(N.C^6H^5.H^2) + CHCl^3 = N^2.(C^6H^5)^2.CH.H + 3HCl$.

3. *Tertiary Diamines.*—They represent 2 mols. ammonia, in which all the hydrogen is replaced; (*a*) by 3 diatomic, (*b*) by 2 diatomic, and 2 monatomic base-radicles.

a. Hofmann has obtained triethylenamine, $N^2.(\overset{''}{C^2}H^4)^3$, by the reaction:

$$3C^2H^4Br^2 + N^2H^6 = 6NHBr + N^2.(C^2H^4)^3.$$

In this group may be classed the compounds known as *hydramides:*

Benzhydramide (hydrobenzamide)	$N^2.(\overset{''}{C^7}H^6)^3$
Salhydramide	$N^2.(\overset{''}{C^7}H^6O)^3$.

They are obtained by the action of ammonia on certain aldehydes:

$$\underset{\text{Benzoic aldehyde.}}{3C^7H^6O} + N^2H^6 = 3H^2O + \underset{\text{Benzhydramide.}}{N^2.(C^7H^6)^3}$$

They are crystalline, insoluble in water, soluble in alcohol, not volatile without decomposition. They are decomposed by hydrosulphuric acid, yielding sulph-aldehydes. (Cahours.)

$$N^2.(C^7H^6)^3 + 3H^2S = N^2H^6 + 3C^7H^6S.$$

The view here taken of the constitution of hydrobenzamide is confirmed by its formation from chlorobenzol, $C^7H^6Cl^2$, and ammonia (Engelhardt), by the manner in which iodide of ethyl reacts upon it (Borodine), and by the existence of a number of bodies obtained from chlorobenzol, which may be regarded as the methylate, ethylate, acetate, valerate, benzoate, &c. of the diatomic radicle C^7H^6.

b. Hofmann has obtained diethylene-diphenylamine, $N^2.(C^2H^4)^2(C^6H^5)^2$, by the action of chloride of ethylene on phenylamine:

$$2(C^2H^4.Cl^2) + 2(N.C^6H^5.H^2) = 4HCl + N^2.(C^2H^4)^2.(C^6H^5)^2.$$

Here too should probably be classed cyanogen, or oxalo-nitrile, N^2C^2, which bears the same relation to normal oxalate of ammonium that acetonitrile does to acetate of ammonium:

$$C^2O^4.(NH^4)^2 - 4H^2O = N^2C^2.$$
$$C^2H^3O^2.NH^4 - 2H^2O = N.C\ H^3;$$

also nitride of boron, N^2B^2.

III. **Triamines.**

1. Primary.
2. Secondary.
3. Tertiary.

They represent 3 molecules of ammonia, in which 3, 6, or 9 atoms of hydrogen are replaced by 1, 2, or 3 triatomic basic radicles.

The only triamine known is Frankland and Kolbe's *Cyanethine*, $C^9H^{15}N^3$, which, according to Hofmann, should be regarded as triglycerylamine, $N^3.(\overset{'''}{C^3}H^5)^3$, a tertiary triamine.

Tetramines and **Pentamines.**—We know but little of any complex ammonia-molecules of a higher order than the triamines; nevertheless it appears that under certain circumstances, four, five, or even a greater number of atoms of ammonia are capable of coalescing into a complex molecule.

The only well characterised tetramines with which we are acquainted are *glycosine*, $N^4.C^6H^6$, a product of the action of ammonia on glyoxal, which may be regarded as $N^4(\overset{'''}{C^2}H^2)^3$, and *hexamethylenamine*, $N^4.C^6H^{12}$, formed by the action of ammonia on dioxymethylene, which may be written $N^4(C^2\overset{''''}{H^4})^3$ (Buttlerow, Bullet. de la Soc. Chim. de Paris, i. 221.) There are also some natural bases containing 4 at. nitrogen, *e.g.* *caffeine*, $C^8H^{10}N^4O^2$, and *theobromine*, $C^7H^8N^4O^2$, but we know nothing of the radicles which they contain.

Pentamines appear to be produced by the action of ammonia on certain metallic oxides. Some of the ammoniacal compounds of cobalt appear to be of this character; but further investigation is necessary to give accurate ideas of their constitution.

PHOSPHINES, ARSINES, STIBINES.—In connection with the basic derivatives of ammonium, we must also mention a class of bodies derived from phosphoretted hydrogen, PH^3, arsenetted hydrogen, AsH^3, and antimonetted hydrogen, SbH^3, by the substitution of alcohol-radicles for the hydrogen. All the compounds thus formed, are basic, like the alcoholic derivatives of ammonia, and form salts of exactly analogous character. Up to the present time, however, the only phosphines, arsines, and stibines, that have been obtained are those in which the whole of the hydrogen in the type is replaced by an equivalent quantity of an alcohol-radicle, *e. g.*:

Triethylphosphine	$P(C^2H^5)^3$
Trimethystibine	$Sb(CH^3)^3$

These bases have not yet been obtained by direct substitution from the hydrides of phosphorus, arsenic and antimony; but they are produced, either by submitting a metallic compound of phosphorus, arsenic, or antimony to the action of the iodides, bromides or chlorides of the alcohol radicles, *e.g.*:

$$\underset{\text{Trisodic arsenide.}}{Na^3As} + \underset{\text{Iodide of ethyl.}}{3C^2H^5I} = 3NaI + \underset{\text{Triethyl-arsine.}}{As(C^2H^5)^3}$$

or, better in most cases, by treating the metallic compounds of the alcohol-radicles with the iodides, bromides, and chlorides of phosphorus, arsenic and antimony; thus,

$$\underset{\text{Zinc-methyl.}}{3CH^3Zn} + PCl^3 = 3ZnCl + \underset{\text{Trimethyl-phosphine.}}{P(CH^3)^3}$$

These compounds, when treated with the bromides or iodides of the alcohol-radicles, behave exactly like the corresponding nitrogen-bases, producing the bromides or iodides of bases containing 4 at. of the alcohol-radicle and belonging to the ammonium type: *e. g.*:

$$\underset{\text{Triethyl-phosphine.}}{P(C^2H^5)^3} + \underset{\text{Iodide of ethyl.}}{C^2H^5I} = \underset{\text{Iodide of ethylphosphonium.}}{P(C^2H^5)^4I}$$

$$\underset{\text{Trimethyl-phosphine.}}{P(CH^3)^3} + C^2H^5I = \underset{\text{Iodide of trimethyl-ethyl-phosphonium.}}{P(CH^3)^3(C^2H^5)I.}$$

The phosphines treated with diatomic bromides (dibromide of ethylene, for example), yield, among other products, the monobromide of a phosphonium-molecule, in which the fourth atom of hydrogen is replaced by a brominated alcohol-radicle; thus triethylphosphine, treated with dibromide of ethylene, yields the *monobromide of bromethyl-triethyl-phosphonium*:

$$P(C^2H^5)^3 + C^2H^4Br^2 = P[(C^2H^4Br)'.(C^2H^5)^3]Br.$$

(See AMMONIUM-BASES.)

ALKALAMIDES.

I. **Monalkalamides** or **Alkalamides.**

1. *Secondary Alkalamides.*—They represent 1 vol. ammonia in which 2 atoms of hydrogen are replaced, one by an acid, the other by a base radicle.

Mercurobenzamide	$N.Hg.C^7H^5O.H.$
Argentosulphophenylamide	$N.Ag.C^6H^5SO^2.H.$
Ethylformamide	$N.C^2H^5.CHO.H.$
Ethylacetamide	$N.C^2H^5.C^2H^3O.H.$
Phenylbenzamide (benzanilide)	$N.C^6H^5.C^7H^5O.H.$
Ethylcyanamide	$N.C^2H^5.CN.H.$

Those which contain metals are formed by the action of primary amides on metallic oxides; they are decomposed by most acids, which remove their metal. Those containing silver are readily attacked by chlorides of acid-radicles, yielding secondary amides and chloride of silver:

$$\underset{\text{Argentosulphophenylamide.}}{N.Ag.C^6HSO^2.H} + \underset{\text{Chloride of benzoyl.}}{C^7H^5O.Cl} = AgCl + \underset{\text{Sulphophenylbenzamide.}}{N.C^6H^5SO^2.C^7H^5O.H.}$$

Those containing organic base-radicles, are formed by the same reactions as primary amides, a primary amine being substituted for ammonia:

1. By action of primary amines on monobasic anhydrides (Gerhardt):

$$\underset{\text{Phenylamine.}}{N.C^6H^5.H^2} + \underset{\text{Benzoic anhydride.}}{(C^7H^5O)^2O} = \underset{\text{Benzoic acid.}}{C^7H^5O.H.O} + \underset{\text{Phenylbenzamide.}}{N.C^6H^5.C^7H^5O.H.}$$

2. By action of primary amines on chlorides of acid-radicles (Gerhardt):

$$\underset{\text{Methylamine.}}{N.CH^3.H^2} + \underset{\text{Chloride of acetyl.}}{C^2H^3O.Cl} = HCl + \underset{\text{Methylacetamide.}}{N.CH^3.C^2H^3O.H}$$

3. By action of primary amines on ethers:

$$\underset{\text{Ethylamine.}}{N.C^2H^5.H^2} + \underset{\text{Acetic ether.}}{C^2H^3O.C^2H^5.O} = \underset{\text{Alcohol.}}{C^2H^5.H.O} + \underset{\text{Ethylacetamide.}}{N.C^2H^5.C^2H^3O.H.}$$

4. By action of monobasic acids on cyanic ethers (Wurtz):

$$\underset{\text{Formic acid.}}{CHN.H.O} + \underset{\text{Cyanate of ethyl.}}{N.C^2H^5.CO} = \underset{\text{Carbonic anhyd.}}{CO.O} + \underset{\text{Ethyl-formamide.}}{N.C^2H^5.CHO.H.}$$

They are crystalline, and generally do not combine with acids; boiled with acids or alkalis, they take up H^2O, and regenerate their acid and primary amine:

$$\underset{\text{Phenylacetamide.}}{N.C^6H^5.C^2H^3O.H} + H^2O = \underset{\text{Phenylamine.}}{N.C^6H^5.H^2} + \underset{\text{Acetic acid.}}{C^2H^3O.H.O.}$$

Those containing cyanogen act as weak alkalis, forming with concentrated acids compounds which are decomposed by water. By heat they are decomposed in rather a peculiar manner, yielding a tertiary alkalamide, and a kind of intermediate dialkalamide, which contains only monatomic radicles:

$$\underset{\text{Ethylcyanamide}}{3(N.C^2H^5.CN.H)} = \underset{\text{Diethylcyanamide.}}{N.(C^2H^5)^2.CN} + \underset{\text{Ethyldicyandiamide.}}{N^2.C^2H^5.(CN)^2.H^3}$$

According to Gerhardt (Ann. Ch. Phys. [3] liii. 307) secondary alkalamides are acted upon by pentachloride of phosphorus in the same way as primary and secondary amides:

$$\underset{\text{Phenyl-benzamide.}}{N.C^6H^5.C^7H^5O.H} + PCl^5 = \underset{\text{Chloride of phenyl-benzamidyl.}}{N(C^7H^5)'''(C^6H^5)Cl} + POCl^3 + HCl.$$

2. *Tertiary Alkalamides.*—They represent 1 molecule of ammonia in which all the hydrogen is replaced; (*a*) by 1 basic and 2 acid monatomic radicles; (*b*) by 2 basic and 1 acid monatomic radicles; (*c*) by 1 basic monatomic, and 1 acid diatomic radicle.

a. H^3 *are replaced by* 1 *basic and* 2 *acid monatomic radicles:*

Ethyl-diacetamide	$N.C^2H^5.(C^2H^3O)^2$
Phenyl-dibenzamide	$N.C^6H^5.(C^7H^5O)^2$

They are formed:—

1. By action of chlorides of acid-radicles on secondary alkalamides (Gerhardt and Chiozza):

$$\underset{\text{Phenylbenzamide.}}{N.C^6H^5.C^7H^5O.H} + \underset{\text{Chloride of benzoyl.}}{C^7H^5O.Cl} = HCl + \underset{\text{Phenyldibenzamide.}}{N.C^6H^5.(C^7H^5O)^2.}$$

2. By action of monobasic anhydrides on cyanic ethers (Wurtz):

$$\underset{\text{Acetic anhydride.}}{(C^2H^3O)^2.O} + \underset{\text{Cyanate of ethyl.}}{N.C^2H^5.CO} = CO.O + \underset{\text{Ethyldiacetamide.}}{N.C^2H^5.(C^2H^3O)^2}$$

They are neutral bodies, combining neither with acids nor with bases.

b. H^3 *are replaced by* 2 *basic and* 1 *acid monatomic radicle:*

Methyl-ethyl-cyanamide	$N.CH^3.C^2H^5.CN$
Diethyl-cyanamide	$N.(C^2H^5)^2.CN.$

The only members of this group hitherto formed, contain cyanogen as the acid-radicle. They are formed by the action of chloride of cyanogen on secondary amines (Cahours and Cloez):

$$\underset{\text{Ethylphenylamine.}}{N.C^2H^5.C^6H^5.H} + CN.Cl = HCl + \underset{\text{Ethylphenylcyanamide.}}{N.C^2H^5.C^6H^5.CN.}$$

They are liquid and volatile without decomposition. Heated with acids or alkalis, they regenerate a secondary amine and cyanic acid, which latter is further decomposed into carbonic anhydride and ammonia:

$$\underset{\text{Diethyl-cyanamide.}}{N.(C^2H^5)^2.CN} + HHO = \underset{\text{Diethylamine.}}{N.(C^2H^5)^2.H} + \underset{\text{Cyanic acid.}}{CN.H.O.}$$

$$\underset{\text{Cyanic acid.}}{N.CO.H} + H^2O = NH^3 + CO.O$$

c. H³ *are replaced by* 1 *monatomic basic, and* 1 *diatomic acid, radicle.*—As these compounds correspond to those secondary amides which are commonly called imides we will retain the same termination for them:

Phenyl-succinimide (succinanile) . . . . . $N.C^6H^5.(C^4H^4O^2)''$
Ethyl-carbimide (cyanic ether) . . . . . . $N.C\,H^5.(CO)''$

With the exception of cyanic ethers, the only members of this group that have been studied are those containing phenyl as their basic radicle; they are commonly called *aniles.* They are obtained by the action of phenylamine on dibasic anhydrides or acids (probably also on the corresponding chlorides):

$$N.C^6H^5.H^2 + \underset{\text{Camphoric anhydride.}}{C^{10}H^{14}O^2.O} = H^2O + \underset{\text{Phenylcamphorimide.}}{N.C^6H^5.C^{10}H^{14}O^2}$$

$$N.C^6H^5.H^2 + \underset{\text{Camphoric acid.}}{C^{10}H^{14}O^2.H^2.O^2} = 2H^2O + N.C^6H^5.C^{10}H^{14}O^2.$$

Boiled with dilute ammonia, they form the ammonium-salt of an amic acid:

$$\underset{\text{Phenylsuccinimide}}{N.C^6H^5.C^4H^4O^2} + NH^4.H.O = \underset{\text{Phenylsuccinamate of ammonium.}}{N.\overbrace{H.C^6H^5.C^4H^4}^{'''}\overbrace{O^2.NH^4}^{''}.O}$$

Fused with potash, they regenerate phenylamine and their acid:

$$N.C^6H^5.C^4H^4O^2 + K^2H^2O^2 = \underset{\text{Succinate of potassium.}}{C^4H^4O^2.K^2.O} + N.C^6H^5.H^2.$$

As cyanic acid may be regarded as carbimide, cyanic ethers may obviously be regarded as alkalimides. With potash they exhibit the same reaction as the foregoing alkalimides:

$$N.C^2H^5.CO + K^2H^2O^2 = CO.K^2.O^2 + N.C^2H^5.H^2.$$

By the action of water or ammonia, they form Dialkalamides (compound ureas):

$$\underset{\text{2 mol. cyanic ether.}}{N^2.(C^2H^5)^2.(CO)^2} + H^2O = CO.O + \underset{\text{Diethylcarbamide.}}{N^2.CO.(C^2H^5)^2.H^2.}$$

$$N.C^2H^5.CO + NH^3 = \underset{\text{Ethylcarbamide.}}{N^2.CO.C^2H^5.H^3.}$$

II. **Dialkalamides.**

There are no primary dialkalamides: but there exists a class of compounds occupying an intermediate place between primary and secondary dialkalamides. They represent 2 mols. of ammonia, in which 3 atoms of hydrogen are replaced, 2 by a diatomic acid-radicle, and 1 by a monatomic base-radicle. With the exception of phenyl-oxamide, $N^2.C^6H^5.C^2O^2.H^3$, the only members of this class are the *compound ureas,* representing urea or carbamide in which 1 H is replaced by a base-radicle:

Ethyl-carbamide (ethyl-urea) . . . . $N^2.(CO)''.C^2H^5.H^3$
Phenyl-carbamide (phenyl-urea) . . . . $N^2.(CO)''.C^6H^5.H^3.$

They are formed by the action of a primary amine on cyanic acid, or of ammonia on cyanic ethers:

$$\begin{aligned} N.C^2H^5.H^2 &+ N.CO.H &= N^2.CO.C^2H^5.H^3 \\ NH^3 &+ N.CO.C^2H^5 &= N^2.CO.C^2H^5.H^3 \end{aligned}$$

They are decomposed by potash, yielding carbonate, a primary amine and ammonia:

$$N^2.CO.C^6H^5.H^3 + H^2.K^2.O^2 = CO.K^2.O^2 + N.C^6H^5.H^2 + NH^3.$$

2. *Secondary Dialkalamides.*—They represent 2 molecules of ammonia in which 4 atoms of hydrogen are replaced by 2 monatomic base-radicles and 1 diatomic acid radicle:

Dimethyloxamide . . . . $N^2.(CH^3)^2.(C^2O^2)''.H^2$
Diphenylsuccinamide . . . . $N^2.(C^6H^5)^2.(C^4H^4O^2)''.H^2$
Diethylcarbamide (diethyl-urea) . . . . . $N^2.(C^2H^5)^2.(CO)''.H^2$

They are formed:

1. By heating the normal salts of organic alkalis:

$$\underset{\text{Oxalate of methylium.}}{C^2O^4(N.CH^3.H^3)^2} - 2H^2O = \underset{\text{Dimethyloxamide.}}{N^2.(CH^3)^2.C^2O^2.H^2}$$

2. By action of primary amines on ethers of dibasic acids:

$$\underset{\text{Oxalate of ethyl.}}{C^2O^2.(C^2H^5)^2.O^2} + \underset{\text{2 mol. methylamine.}}{N^2.(CH^3)^2.H^4} = \underset{\text{2 mol. alcohol.}}{(C^2H^5)^2.H^2.O^2} + \underset{\text{Dimethyloxamide.}}{N^2.(CH^3)^2.C^2O^2.H^2}.$$

3. By action of primary amines on chlorides of acid-radicles:

$$\underset{\text{2 mol. phenylamine.}}{N^2.(C^6H^5)^2.H^2.H^2} + \underset{\text{Chloride of carbonyl.}}{CO.Cl^2} = 2HCl + \underset{\text{Diphenylcarbamide.}}{N^2.(C^6H^5)^2.CO.H^2}.$$

The compound ureas (alkal-carbamides) belonging to this group are also formed by the action of water on cyanic ethers:

$$\underset{\text{Cyanate of ethyl.}}{2(N.CO.C^2H^5)} + H^2O = CO.O + \underset{\text{Diethylcarbamide.}}{N^2.(C^2H^5)^2.CO.H^2}.$$

All these secondary dialkalamides are decomposed by potash, yielding a primary amine, and the normal potassium-salt of their acid:

$$\underset{\text{Diethyloxamide.}}{N^2.(C^2H^5)^2.C^2O^2.H^2} + H^2K^2O^2 = \underset{\text{2 mols. ethylamine.}}{N^2.(C^2H^5)^2.H^4} + \underset{\text{Oxalate potass.}}{C^2O^2.K^2.O^2}$$

Hofmann regards melaniline, $C^{13}H^{13}N^3$, and a compound, $C^{19}H^{17}N^3$, which he has obtained by the action of dichloride of carbon on phenylamine, as cyan-diphenyldiamide, $N^2.CN.(C^6H^5)^2.H^3$, and cyantriphenyldiamide, $N^2.CN.(C^6H^5)^3.H^2$, respectively,—*i. e.* as dialkalamides containing only monatomic radicles. Considering the reaction by which the latter at least of these compounds is formed, it may perhaps be preferable to regard it as deriving from 3 molecules of ammonia, in which a portion of the hydrogen is replaced by the tetratomic radicle, C'''' viz. as $N^3.C.(C^6H^5)^3.H^2$.

Pebal has described the following compounds, intermediate between secondary and tertiary dialkalamides:

Diphenylcitrimide . . . . . . $N^2.(C^6H^5)^2.(C^6H^5O^4)'''.H$
Diphenylaconitimide . . . . . . $N^2.(C^6H^5)^2.(C^6H^3O^3)'''.H.$

They correspond to the monacid phenylium-salts of tribasic acids, less the elements of 3 atoms of water:

$$C^6H^5O^7(N.C^6H^5.H^3)^2H - 3H^2O = N^2.(C^6H^5)^2.C^6H^5O^4.H.$$

3. *Tertiary Dialkalamides.*—They represent 2 molecules of ammonia in which all the hydrogen is replaced by base- and acid-radicles, one of which at least must be polyatomic. This process is represented by compound-ureas, in which all the hydrogen is replaced by basic radicles,—*e.g.* Tetrethylcarbamide or tetrethyl-urea, $N^2.(CO)''.(C^2H^5)^4$. Also by Buff's sulphocyanide of ethylene (ethylene-disulphocarbamide) $N^2.(CS)^2.(C^2H^4)''$. obtained by boiling chloride of ethylene with an alcoholic solution of sulphocyanate of potassium (Proc. Roy. Soc. viii. 188), and by Hofmann's diphenylcarboxamide, $N^2.(CO)''.(C^2O^2)(C^6H^5)^{2''}$, obtained by the action of dilute hydrochloric acid on dicyanmelaniline.

$$C^{15}H^{13}N^5 + 3HCl + 3H^2O = 3NH^4Cl + N^2.CO.C^2O^2.(C^6H^5)^2$$

More might probably be obtained by the action of secondary amines on chlorides of acid radicles, or on ethers of dibasic acids:

$$2(N.(CH^3)^2.H) + C^4H^4O^2.Cl^2 = 2HCl + \underset{\text{Tetramethylsuccinamide.}}{N^2.(CH^3)^4.C^4H^4O^2}.$$

$$2[N.(C^2H^5)^2.H] + \underset{\text{Succinate of ethyl.}}{C^4H^4O^2.(C^2H^5)^2.O^2} = 2(C^2H^5.H.O) + \underset{\text{Tetrethylsuccinamide.}}{N^2.(C^2H^5)^4.C^4H^2O^2}$$

III. **Trialkalamides.**

1. *Secondary Trialkalamides.*—They correspond to 3 molecules of ammonia, in which 6 atoms of hydrogen are replaced by 1 triatomic acid-radicle and 3 monatomic base-radicles. Examples are Pebal's triphenylcitramide, $N^3.(C^6H^5)^3.(C^6H^5O^4)'''.H^3$, obtained by the action of citric acid on phenylamine:

$$C^6H^5O^4.H^3.O^3 + 3(N.C^6H^5.H^2) = N^3.(C^6H^5)^3.C^6H^5O^4.H^3 + 3H^2O$$

It corresponds to the normal citrate of phenylium, less the elements of 3 atoms of water. Also Schiff's triphenylphosphamide, $N^3.(C^6H^5)^3.PO.H^3$, and trinaphtylphosphamide, $N^3.(C^{10}H^7)^3.PO.H^3$, obtained by the action of phenylamine and naphtylamine respectively on oxychloride of phosphorus (Ann. Ch. Pharm. ci. 300):

$$POCl^3 + 3(N.C^6H^5.H^2) = N^3.(C^6H^5)^3.PO.H^3. + 3HCl.$$

2. *Tertiary Trialkalamides.*—The cyanuric ethers may be placed in this division, *e. g.* cyanurate of ethyl, $N^3.(\overset{''}{C}O)^3.(C^2H^5)^3$.—F. T. C.

AMMELIDE and **AMMELINE.** See CYANURAMIC ACIDS.

AMMIOLITE. A red earthy mass from Chile, containing 36·5 antimony, 14·8 tellurium, 12·2 copper, 22·2 mercury, and 2·5 quartz, besides oxygen; probably a mixture. (*Rammelsberg's Mineralchemie*, p. 426.)

AMMONIA. NH^3. (Synonymes, *Volatile alkali*, *Alkaline air*, *Ammoniacal gas*, *Ammoniaque*, *Ammoniak.*)

History. — The earliest mention of aqueous ammonia, which was known long before the gas itself, is made by Raymond Lully, in the thirteenth century: he prepared it from urine, and called it *Mercurius vel spiritus animalis.* Basil Valentine, in the fifteenth century, first prepared it from sal-ammoniac: he still retained the name *spiritus urinæ.* It was Bergman (1782) who first designated it by the name *ammonia.* Ammoniacal gas was discovered by Priestley, who describes it in 1774 by the name of *alkaline air;* he also observed its decomposition by the electric spark. Scheele, in 1777, ascertained that it contained nitrogen, regarding it as a compound of nitrogen and phlogiston. Its true composition was first ascertained by Berthollet (1785); and it was finally analysed with still greater exactness, by his son Am. Berthollet in 1808.

Natural Sources. — Ammonia exists in the air as carbonate of ammonium: in rain-water, especially in that of thunder-showers, as nitrate. In sea-water, and in many mineral springs. In most kinds of clay and soils: in sesquioxide of iron, and in the majority of iron-ores. Sal-ammoniac and ammonium-alum are found as minerals, the former chiefly in volcanic regions, and in some specimens of rock-salt. As ammoniacal-salts, in animal fluids and excrements (especially in urine), and in the juices of many plants.

Formation. — Ammonia cannot be formed by the direct combination of its elements in the free state. When 1 vol. nitrogen and 3 vols. hydrogen are passed through a red-hot tube, no ammonia is formed, not even if spongy platinum be present. But it is formed with great readiness by the combination of its elements, when one or both of them is in the *nascent* state: *i. e.* at the moment of its liberation from another compound: and in this manner ammonia may be formed from many substances, organic and inorganic.

1. *From inorganic substances.* — On igniting a mixture of oxygen, nitrogen, and excess of hydrogen, nitrate of ammonium is formed. (Th. Saussure.)

a. *Formation from nascent hydrogen and free nitrogen.* — Water containing atmospheric air yields nitric acid at the positive pole, and ammonia at the negative pole of a voltaic battery (Sir H. Davy). Moistened iron-filings, in contact with atmospheric air or nitrogen at the ordinary temperature, induce the formation of ammonia (Chevallier, Berzelius). (Will states that no ammonia is thus formed.) This reaction accounts for the existence of ammonia in rust of iron, and iron ores generally. When liver of sulphur is fused with an equal weight of iron-filings, and water dropped on the hot mass, ammonia is evolved (Hollunder). When certain metals which combine readily with oxygen (potassium, arsenic, lead, iron, &c.) are heated with the hydrates of potassium, sodium, barium, or calcium, in contact with air, ammonia is formed. Faraday states that this formation of ammonia takes place even in an atmosphere of hydrogen: a fact explained by Bischof as arising from the difficulty of obtaining hydrogen free from atmospheric air. Reiset also points out that the hydrogen will contain nitric oxide, if the sulphuric acid employed for its generation contains nitric acid or nitric oxide.

b. *Formation from nascent nitrogen and free hydrogen.*— A mixture of 2 vols. nitric oxide and 5 vols. hydrogen passed over gently heated spongy platinum, yields ammonia and water (Hare; Ville, Ann. Ch. Phys. [3] xlvi.) The same gases when passed through a red-hot tube, only yield ammonia when some porous substance is present; pumice-stone, or ferric oxide acts most energetically (Reiset). Nitrous oxide and hydrogen in excess yield ammonia when in contact with hot spongy platinum or platinum-black. Hydrogen saturated with nitric acid vapour acts in a similar manner.

c. *Formation from nascent hydrogen and nascent nitrogen.* — Moist nitric oxide passed over heated iron-filings yields ammonia. A mixture of nitric oxide and hydrosulphuric acid, passed over heated soda-lime, yields ammonia (Ville). Certain metals which decompose water at a high temperature (iron, zinc, &c.), when treated with dilute nitric acid, or the aqueous solutions of certain nitrates, yield ammonia. Ammonia is formed when nitric acid is added to zinc and sulphuric acid in a hydrogen apparatus, also by the decomposition of chloride, iodide, and phosphide of nitrogen, and of all bodies belonging to the class, amides, by water. When a mixture of baryta and carbonaceous matter is heated in contact with air, cyanide of barium is formed, a compound which is decomposed by steam at 300° C. into carbonate of barium and ammonia: Margueritte and Sourdeval have lately proposed to employ this process for the preparation of ammonia on the large scale. (Rep. Chim. App. ii. 170.)

2. *From organic substances.*—Many *non-nitrogenous* organic bodies form ammonia by prolonged contact with air and water: *e.g.* in the process of putrefaction. Sugar, oxalates, tartrates, &c. yield ammonia when heated with alkaline or alkaline-earthy hydrates, in contact with air. Oxygen-compounds of nitrogen, heated with organic reducing agents, *e.g.* nitric oxide with alcohol-vapour, nitric acid with gum, form ammonia. Most *nitrogenised* organic compounds yield ammonia, either free or combined, in the processes of putrefaction or of dry distillation: it is from this source that the ammonia existing in nature is chiefly derived.

Preparation.—Powdered sal-ammoniac is mixed with twice its weight of slaked lime, the mixture covered with a layer of coarsely powdered quick lime, about equal in weight to the sal-ammoniac used, and the whole heated gradually in a flask or retort: for the preparation of ammonia on a large scale, iron vessels are used. The gas is passed through a two-necked bottle, in which aqueous vapour is condensed, and any solid particles that may be carried over are arrested; it is then dried by passing over solid potash or quick lime—or better, a mixture of the anhydrous oxides of potassium and copper, obtained by heating nitrate of potassium with finely divided copper reduced from the oxide by hydrogen (Stas), (chloride of calcium absorbs the gas)—and collected over mercury. If the gas is pure, it should be entirely absorbed by water. In order to obtain perfectly dry ammonia, Vogel recommends saturating a concentrated aqueous solution of ammonia with solid chloride of calcium, heating gently, and passing the gas over solid potash.

Properties.—Colourless gas, of a pungent smell, and strong alkaline taste. Its specific gravity is (calculated) 0·5893; (H. Davy) 0·5901; (Thomson) 0·5931; (Biot and Arago) 0·5967. 1 litre at 0° C. and 760mm. barometric pressure weighs 0·7752 grm. (Biot and Arago). Its specific heat (water = 1) is 0·508 (Regnault). Its refractive power (air = 1) is 1·309 (Dulong).

It does not support either combustion or respiration: animals die when immersed in it. It is feebly combustible: when issuing in a thin stream into atmospheric air, it may be kindled, and burns with a pale flame. It colours turmeric paper brown, and reddened litmus blue: the colours disappear on exposure to the air.

It may be condensed by cold and pressure, and obtained both in the liquid and solid form. Faraday prepares liquid ammonia as follows: Ammonio-chloride of silver is introduced into a very strong glass tube, closed at one end, which is then bent at an acute angle, the chloride being in the longer limb. The shorter limb is then sealed and immersed in ice, and the chloride gradually heated: it fuses at 38° C., and between 112° and 119° C. gives off all its ammonia, which condenses to a liquid by its own pressure in the cool part of the tube. As the chloride of silver cools, the liquid ammonia boils violently, and is reabsorbed by the chloride. Guyton de Morveau and Bunsen have condensed ammonia without pressure by a mixture of chloride of calcium and ice, the former at 52° C., the latter at −40°. Liquid ammonia is a colourless, very mobile liquid, refracting light more powerfully than water; specific gravity 0·76: boiling-point at 749mm. barometic pressure, −33·7° C. (Bunsen.) Its tension at −17·78° C. = 2·48 atmospheres: at 0° C. = 4·44 atm.: at 10·8° C. = 6 atm.: at 19·44° C. = 7·60 atm.: at 28·31° C. = 10 atm.

Faraday has obtained solid ammonia by exposing the dry gas to a pressure of 20 atmospheres and to a cold of —75° C., produced by solid carbonic anhydride and ether. It is a white, transparent, crystalline body, which melts at −75° C., and has a higher specific gravity than liquid ammonia.

Decompositions.—Dry ammonia is decomposed by a succession of electric sparks: the resulting gas is double the volume of the original gas, and consists of 1 vol. nitrogen and 3 vols. hydrogen. Also by being passed through a red-hot porcelain tube containing copper or iron wire; gold-, silver-, or platinum-wire acts similarly, but less energetically. No change is produced in the gold and platinum-wire: the copper and iron wire are rendered brittle, and sometimes increased in weight, owing to the formation of a nitride.—2 vols. ammonia mixed with not less than 1, nor more than 6 vols. oxygen, are exploded by the electric spark: the products, if the oxygen be in excess, are water and nitrate of ammonium; if the ammonia be in excess, water, nitrogen, and hydrogen.—Aqueous ammonia, in contact with finely divided copper or platinum, and *oxygen* or *atmospheric air*, is converted into nitrite of ammonium, both its constituents undergoing oxidation (Handwb.)—Ammonia is decomposed by several of the oxygen-compounds of chlorine and nitrogen. Dry ammonia mixed with dry *hypo-*

chlorous anhydride explodes violently at the ordinary temperature, with separation of chlorine. Aqueous ammonia added gradually to aqueous *hypochlorous acid*, the mixture being kept cool, yields nitrogen, and chloride of nitrogen. Ammonia mixed with proper proportions of *nitrous or nitric oxide*, explodes by the electric spark, yielding water and nitrogen. Ammonia is violently decomposed at the ordinary temperature by *peroxide of nitrogen*, whether liquid or gaseous, with evolution of nitric oxide and nitrogen (Dulong).—In contact with *chlorine* in the cold, ammonia burns with a red and white flame, forming chloride of ammonium and free nitrogen ($4NH^3 + Cl^3 = 3NH^4Cl + N$); when chlorine is passed into strong aqueous ammonia or a solution of an ammoniacal-salt, chloride of nitrogen is also formed. — *Iodine* does not decompose dry ammonia: in presence of water, iodide of ammonium and an iodine-derivative of ammonia are formed.—With *bromine*, ammonia yields bromide of ammonium and free nitrogen.—Passed with vapour of *phosphorus* through a red-hot tube, ammonia yields phosphide of hydrogen and free nitrogen.—Passed over red-hot *charcoal*, ammonia yields cyanide of ammonium and free hydrogen.—With *bisulphide of carbon*, ammonia gives hydrosulphuric and sulphocyanic acids ($NH^3 + CS^2 = H^2S + CNSH$).—When *potassium* or *sodium* is heated in dry ammonia, hydrogen is evolved, its place being supplied by the metal, and nitride of potassium and hydrogen (potassamine), NKH^2, is formed.—In contact with zinc-ethyl, ammonia gives zinc-amine $NZnH^2$ and hydride of ethyl, C^2H^6. Many *metallic oxides* decompose ammonia with the aid of heat: the products are sometimes water, nitrogen, reduced metal, and more or less of an oxygen-compound of nitrogen; sometimes, water and a metallic nitride.—Ammonia reacts with anhydrous acids, chlorides of acid-radicles, and many compound ethers, giving *amic acids*, or *amides*. In like manner, it gives with many derivatives of the alcohols, *amic bases* or *amines*. (See AMIC ACIDS, AMIC BASES, AMIDES, AMINES.)

We have seen that ammonia is decomposed by certain metals and metallic oxides, hydrogen being liberated, and compounds formed representing ammonia in which a part or the whole of the hydrogen is replaced by a metal. There are certain organic compounds (*e. g.* monobasic anhydrides, compound ethers, &c.) which are capable of decomposing ammonia in a similar manner, with formation of compounds representing ammonia in which the hydrogen is wholly or partially replaced by an organic radicle, acid or basic. The numerous and interesting class of compounds which are thus formed from ammonia by the partial or total replacement of its hydrogen by other radicles, organic or inorganic, acid or basic, is known by the generic name of *amides*: under which name they are fully described.

Combinations.—1. *With Water* (*Solution of ammonia, Aqueous ammonia*, or simply *Ammonia, Spirits of hartshorn, Salmiakgeist, Liquor ammonii*).

Both water and ice absorb ammonia with great avidity, with considerable evolution of heat, and with great expansion. Davy found that 1 vol. water at 10° C. and 29·8 inches barometric pressure absorbs 670 vols. ammonia, or nearly half its weight: the specific gravity of this solution is 0·875. According to Dalton, water at a lower temperature absorbs even more ammonia, and the specific gravity of the solution is 0·85. According to Osann, 100 pts. water at 24° C. absorb 8·41 pts. at 55° C. 5·96 pts. ammonia. 1 vol. water by absorbing 505 vols. ammonia, forms a solution occupying 1·5 vols., and having specific gravity 0·9: this, when mixed with an equal bulk of water, yields a liquid of specific gravity 0·9455: whence it appears that aqueous ammonia expands on dilution. (Ure.)

Preparation.—1 part of sal-ammoniac in lumps is introduced into a glass flask, with $1\frac{1}{4}$ parts slaked lime, and from 1 to $1\frac{1}{2}$ parts water: and the flask is connected by bent tubes with three Woulfe's bottles. The first bottle, which is intended to arrest any solid particles that may be carried over mechanically, and any empyreumatic oil contained in the sal-ammoniac, as well as to condense aqueous vapour, contains a small quantity of water (Mohr prefers milk of lime). The second bottle contains the water to be saturated with ammonia: it should contain a quantity of water about equal in weight to the sal-ammoniac employed, and should not be more than three parts full, to allow for the expansion. These two bottles should be placed in cold water, and each provided with a safety tube. The third bottle contains a little water, to retain any ammonia that may pass through the second bottle. The flask is then heated in a sand-bath, care being taken that its contents do not boil over: and the operation continued till about half the water in the flask has distilled over into the first bottle. The first bottle then contains a weak and impure solution of ammonia: the second a pure and strong solution (if a perfectly saturated solution be required, the quantity of water in this bottle should not exceed $\frac{2}{3}$ the weight of the sal-ammoniac employed): the solution in the third bottle is weak, but pure.

The proportions of lime and water to be added to the sal-ammoniac in order to produce the largest yield of ammonia have been variously stated: those given above are now most generally received. According to the equation, $CaHO + NH^4Cl = NH^3 + CaCl + H^2O$, the amount of slaked lime should be to that of sal-ammoniac as 37 : 53·5, or 69 parts of the former to 100 parts of the latter. But in practice it is always found necessary to employ a larger proportion of lime; for not only is the lime of commerce always impure, but also it is impossible to bring the whole of it into such contact with the sal-ammoniac, as would ensure the completeness of their reaction. The object of adding water is to ensure the gradual solution of the sal-ammoniac, and consequently its more complete contact with the lime. There are also other disadvantages which attend the absence of water. If the lime and sal-ammoniac are mixed in a state of powder, a large quantity of ammonia is lost before the mixture is introduced into the flask; and the heated mass expands on cooling so as invariably to break the flask. These inconveniences are avoided by first placing the sal-ammoniac in lumps in the flask, and then covering it with the powdered lime: but in this case the heat required is sufficient to volatilise the sal-ammoniac, which is liable to stop up the delivery-tube and cause a dangerous explosion. Moreover a larger quantity of empyreumatic oil passes over with the ammonia: and the chloride of calcium formed in the flask obstinately retains a portion of the ammonia, which is consequently lost. On the other hand, the addition of too much water diminishes the product of ammonia, and hampers the operation in other ways.

In the preparation of aqueous ammonia on a large scale, the gas is generated in cast-iron or copper vessels: earthenware vessels are generally found not to answer, owing to the porosity of their structure.

The aqueous ammonia thus prepared may contain the following impurities, which are easily detected:

Carbonate of ammonium.—Occurs when the lime employed contains much carbonate, or when the solution has been exposed to the air. Causes turbidity when heated with chloride of barium.

Chlorine.—Owing to chloride of ammonium having been sublimed, or carried over mechanically. The solution, saturated with nitric acid, gives a cloudiness with nitrate of silver.

Lime.—Carried over mechanically. Gives a precipitate with oxalic acid: left as a solid residue on evaporation.

Copper or *Lead.*—Derived from the generating vessel. The former is detected by the solution becoming tinged with blue on evaporation; the latter by hydrosulphuric acid.

Empyreumatic oil.—From the sal-ammoniac. The solution has a yellow colour and a peculiar smell.

Properties.—Aqueous ammonia is a colourless transparent liquid, smelling of ammonia, and having a sharp burning, urinous taste. Its specific gravity varies from 1·000 to 0·85, according to the amount of ammonia it contains: its boiling-point varies similarly (see Dalton's table, *infra.*) A perfectly saturated solution freezes between −38° and −41° C., forming shining flexible needles: at −49° C. it solidifies to a grey gelatinous mass, almost without smell (Fourcroy and Vauquelin). It loses almost all its ammonia at a temperature below 100° C. The following tables have been constructed, showing the amount of real ammonia contained in aqueous ammonia of different densities:

Dalton.			H. Davy.		Ure.			
Specific gravity.	Percentage Ammonia.	Boiling Point	Specific gravity.	Percentage Ammonia.	Specific gravity.	Percentage Ammonia.	Specific gravity.	Percentage Ammonia.
0·85	35·3	−4°	0·8750	32·3*	0·8914	27·940	0·9363	15·900
0·86	32·6	+3·5°	0·8857	29·25	0·8937	27·633	0·9410	14·575
0·87	29·9	10°	0·9000	26·00	0·8967	27·038	0·9455	13·250
0·88	27·3	17°	0·9054	25·37*	0·8983	26·751	0·9510	11·925
0·89	24·7	23°	0·9166	22·07	0·9000	26·500	0·9564	10·600
0·90	22·2	30°	0·9255	19·54	0·9045	25·175	0·9614	9·275
0·91	19·8	37°	0·9326	17·52	0·9090	23·850	0·9662	7·950
0·92	17·4	44°	0·9385	15·88	0·9133	22·525	0·9716	6·625
0·93	15·1	50°	0·9435	14·53	0·9177	21·200	0·9768	5·300
0·94	12·8	57°	0·9476	13·46	0·9227	19·875	0·9828	3·975
0·95	10·5	63°	0·9513	12·40	0·9275	18·550	0·9887	2·650
0·96	8·3	70°	0·9545	11·56	0·9320	17·225	0·9945	1·325
0·97	6·2	79°	0·9573	10·82				
0·98	4·1	87°	0·9597	10·17				
0·99	2·0	92°	0·9616	9·60				
			0·9692	9·50*				

* These numbers were determined by experiment: the rest in Davy's table by calculation.

J. Otto. Determinations made at 16° C.

Specific gravity.	Percentage Ammonia.	Specific gravity.	Percentage Ammonia.	Specific gravity.	Percentage Ammonia.
0·9517	12·000	0·9607	9·625	0·9697	7·250
0·9521	11·875	0·9612	9·500	0·9702	7·125
0·9526	11·750	0·9616	9·375	0·9707	7·000
0·9531	11·625	0·9621	9·250	0·9711	6·875
0·9536	11·500	0·9626	9·125	0·9716	6·750
0·9540	11·375	0·9631	9·000	0·9721	6·625
0·9545	11·250	0·9636	8·875	0·9726	6·500
0·9550	11·125	0·9641	8·750	0·9730	6·375
0·9555	11·000	0·9645	8·625	0·9735	6·250
0·9556	10·950	0·9650	8·500	0·9740	6·125
0·9559	10·875	0·9654	8·375	0·9745	6·000
0·9564	10·750	0·9659	8·250	0·9749	5·875
0·9569	10·625	0·9664	8·125	0·9754	5·750
0·9574	10·500	0·9669	8·000	0·9759	5·625
0·9578	10·375	0·9673	7·875	0·9764	5·500
0·9583	10·250	0·9678	7·750	0·9768	5·375
0·9588	10·125	0·9683	7·625	0·9773	5·250
0·9593	10·000	0·9688	7·500	0·9778	5·125
0·9597	9·875	0·9692	7·375	0·9783	5·000
0·9602	9·750				

L. Carius. (Ann. Ch. Pharm. xcix. 164.) Determinations made at 14° C.

Specific gravity.	P. C. Amm.	Specific gravity.	P. C. Amm.	Specific gravity.	P. C. Amm.	Specific gravity.	P. C. Amm.	Specific gravity.	P. C. Amm.	Specific gravity.	P. C. Amm.
0·8844	36·0	0·8976	30·0	0·9133	24·0	0·9314	18·0	0·9520	12·0	0·9749	6·0
0·8848	35·8	0·8981	29·8	0·9139	23·8	0·9321	17·8	0·9527	11·8	0·9757	5·8
0·8852	35·6	0·8986	29·6	0·9145	23·6	0·9327	17·6	0·9534	11·6	0·9765	5·6
0·8856	35·4	0·8991	29·4	0·9150	23·4	0·9333	17·4	0·9542	11·4	0·9773	5·4
0·8860	35·2	0·8996	29·2	0·9156	23·2	0·9340	17·2	0·9549	11·2	0·9781	5·2
0·8864	35·0	0·9001	29·0	0·9162	23·0	0·9347	17·0	0·9556	11·0	0·9790	5·0
0·8868	34·8	0·9006	28·8	0·9168	22·8	0·9353	16·8	0·9563	10·8	0·9799	4·8
0·8872	34·6	0·9011	28·6	0·9174	22·6	0·9360	16·6	0·9571	10·6	0·9807	4·6
0·8877	34·4	0·9016	28·4	0·9180	22·4	0·9366	16·4	0·9578	10·4	0·9815	4·4
0·8881	34·2	0·9021	28·2	0·9185	22·2	0·9373	16·2	0·9586	10·2	0·9823	4·2
0·8885	34·0	0·9026	28·0	0·9191	22·0	0·9380	16·0	0·9593	10·0	0·9831	4·0
0·8889	33·8	0·9031	27·8	0·9197	21·8	0·9386	15·8	0·9601	9·8	0·9839	3·8
0·8894	33·6	0·9036	27·6	0·9203	21·6	0·9393	15·6	0·9608	9·6	0·9847	3·6
0·8898	33·4	0·9041	27·4	0·9209	21·4	0·9400	15·4	0·9616	9·4	0·9855	3·4
0·8903	33·2	0·9047	27·2	0·9215	21·2	0·9407	15·2	0·9623	9·2	0·9863	3·2
0·8907	33·0	0·9052	27·0	0·9221	21·0	0·9414	15·0	0·9631	9·0	0·9873	3·0
0·8911	32·8	0·9057	26·8	0·9227	20·8	0·9420	14·8	0·9639	8·8	0·9882	2·8
0·8916	32·6	0·9063	26·6	0·9233	20·6	0·9427	14·6	0·9647	8·6	0·9890	2·6
0·8920	32·4	0·9068	26·4	0·9239	20·4	0·9434	14·4	0·9654	8·4	0·9899	2·4
0·8925	32·2	0·9073	26·2	0·9245	20·2	0·9411	14·2	0·9662	8·2	0·9907	2·2
0·8929	32·0	0·9078	26·0	0·9251	20·0	0·9419	14·0	0·9670	8·0	0·9915	2·0
0·8934	31·8	0·9083	25·8	0·9257	19·8	0·9456	13·8	0·9677	7·8	0·9924	1·8
0·8938	31·6	0·9089	25·6	0·9264	19·6	0·9463	13·6	0·9685	7·6	0·9932	1·6
0·8943	31·4	0·9094	25·4	0·9271	19·4	0·9470	13·4	0·9693	7·4	0·9941	1·4
0·8948	31·2	0·9100	25·2	0·9277	19·2	0·9477	13·2	0·9701	7·2	0·9950	1·2
0·8953	31·0	0·9106	25·0	0·9283	19·0	0·9484	13·0	0·9709	7·0	0·9959	1·0
0·8957	30·8	0·9111	24·8	0·9289	18·8	0·9491	12·8	0·9717	6·8	0·9967	0·8
0·8962	30·6	0·9116	24·6	0·9296	18·6	0·9498	12·6	0·9725	6·6	0·9975	0·6
0·8967	30·4	0·9122	24·4	0·9302	18·4	0·9505	12·4	0·9733	6·4	0·9983	0·4
0·8971	30·2	0·9127	24·2	0·9308	18·2	0·9512	12·2	0·9741	6·2	0·9991	0·2

By the aid of these tables, the strength of aqueous ammonia, like that of commercial alcohol, may be approximately ascertained by taking its specific gravity. (See also Griffin's Table given in *Ure's Dictionary of Arts, Manufactures, and Mines*, vol. i. p. 132, and Chem. Soc. Qu. J. iii. 260.)

Roscoe and Dittmar (Chem. Soc. Qu. J. xii. 147), have determined the amount of ammonia-gas absorbed by water at various pressures and temperatures. The results are given in the two following tables.

Table A shows the weight of ammonia-gas in grammes G absorbed by 1 gramme of water at 0° C. and various *partial* pressures P.*

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* By partial pressure is meant the total pressure under which the absorption occurs, *minus* the tension of aqueous vapour at 0° C.

TABLE A.

P.	G.	P.	G.	P.	G.	P.	G.
0·00	0·000	0·25	0·465	0·85	0·937	1·45	1·469
0·01	0·044	0·30	0·515	0·90	0·968	1·50	1·526
0·02	0·084	0·35	0·561	0·95	1·001	1·55	1·584
0·03	0·120	0·40	0·607	1·00	1·037	1·60	1·645
0·04	0·149	0·45	0·646	1·05	1·075	1·65	1·707
0·05	0·175	0·50	0·690	1·10	1·117	1·70	1·770
0·75	0·228	0·55	0·731	1·15	1·161	1·75	1·835
0·100	0·275	0·60	0·768	1·20	1·208	1·80	1·906
0·125	0·315	0·65	0·804	1·25	1·258	1·85	1·976
0·150	0·351	0·70	0·840	1·30	1·310	1·90	2·046
0·175	0·388	0·75	0·872	1·35	1·361	1·95	2·120
0·200	0·411	0·80	0·906	1·40	1·415	2·00	2·195

From these numbers it appears: (1) that the quantity of ammonia absorbed by water at 0° C. is far from being proportional to the pressure; and (2) that for equal increments of pressure up to about 1 metre of mercury, the corresponding increments of absorbed ammonia continually diminish, but that above this point, the amount of dissolved gas increases in a more rapid ratio than the pressure.

Table B shows the weight in grammes of ammonia (column II.), absorbed by 1 gramme of water under the pressure of 0·76^m. and at various temperatures (column I).

TABLE B.

I.	II.	I.	II.	I.	II.	I.	II.
0° C.	0·875	16° C.	0·582	32° C.	0·382	48° C.	0·244
2°	0·833	18°	0·554	34°	0·362	50°	0·229
4°	0·792	20°	0·526	36°	0·343	52°	0·214
6°	0·751	22°	0·499	38°	0·324	54°	0·200
8°	0·713	24°	0·474	40°	0·307	56°	0·186
10°	0·679	26°	0·449	42°	0·290		
12°	0·645	28°	0·426	44°	0·275		
14°	0·612	30°	0·403	46°	0·259		

Aqueous ammonia possesses the property of dissolving many salts which are insoluble in water. Thus it dissolves chromic and stannic oxides, the protoxides of tin, cadmium, zinc, &c., the oxides of copper and silver. The compounds thus formed are decomposed by heat, losing ammonia, sometimes with explosive violence. Many other salts are also soluble in aqueous ammonia, *e. g.* phosphate, chloride, bromide of silver, &c.: in some cases, the original salt can be recovered unchanged by evaporating off the ammonia; in others a more intimate combination is effected.

2. *With alcohol.* (Liquor ammoniaci alcoholicus).

Alcohol, like water, absorbs ammonia in great quantity, with considerable expansion and evolution of heat. The alcoholic solution is prepared in precisely the same way as the aqueous solution, alcohol of 85—90 p. c. being substituted for water in the second bottle. The proportion of alcohol to the sal-ammoniac employed should be somewhat less than in the case of water. The specific gravity of the solution of course varies with the amount of alcohol and ammonia which it contains.

3. *With metallic salts.* Ammonia forms solid compounds with certain metallic oxides (of gold, silver, platinum, mercury, antimony, &c.) which are decomposed by heat, frequently with explosive violence. Certain metallic chlorides, bromides, and iodides (of silver, calcium, &c.) absorb ammonia, frequently with evolution of heat. Some of these compounds lose their ammonia when exposed to the air; others, but not all, when heated. Some dissolve in water without decomposition, forming solutions from which the whole of the ammonia is not precipitated by dichloride of platinum: the majority are decomposed by water, which sometimes dissolves the original salt and separates ammonia, sometimes precipitates the metal as hydrate. Similarly, certain crystalline salts, when freed from their water of crystallisation, absorb ammonia abundantly and in atomic proportion, forming compounds which are decomposed by heat or by water. Ammonia also combines with metallic cyanides, with fluoride of silicon, and other bodies.

4. *With acids*, forming *ammoniacal salts.* (See AMMONIACAL SALTS.)

5. *With polybasic anhydrides*, forming the ammonium-salts of amic acids. (See AMIC ACIDS.)

F. T. C.

AMMONIACAL SALTS. *Ammonium-salts, Sels ammoniacaux, Ammoniaksalze.*

Ammonia combines very readily with acids, which it neutralises completely, forming definite crystalline salts, known by the name of ammoniacal or ammonium-salts. These salts are isomorphous with those of potassium, and are in their general properties so closely analogous to metallic salts, that they are universally regarded as belonging to this class of bodies. There is, however, a characteristic difference in their mode of formation. While other metallic salts are formed by the substitution of a metal for the hydrogen of an acid, *e.g.* chloride of zinc, $ZnCl = HCl + Zn - H$: ammoniacal salts are formed by the direct combination of ammonia with the acid, without elimination of hydrogen,—*e.g.* chloride of ammonium, $NH^4Cl = NH^3 + HCl$.

Among the various theories by which it has been proposed to represent the constitution of these salts, that which most clearly expresses their analogy with other metallic salts is unquestionably the *Ammonium Theory* of Berzelius. According to this theory, ammoniacal salts contain a compound metal, *ammonium*, NH^4, analogous to potassium, sodium, and other metals, the salts of which, *ammonium-salts*, are analogous to other metallic salts. Thus, chloride of ammonium, $ClNH^4$, is analogous to chloride of potassium, ClK; sulphate of ammonium, $SO^4(NH^4)^2$, to sulphate of potassium, SO^4K^2, &c. This hypothetical metal has never been isolated. An amalgam of mercury and ammonium is, however, known to exist, which affords strong corroborative evidence, not only of the existence of ammonium, but also of its metallic nature, metals being the only bodies which are capable of forming amalgams with mercury. This singular substance, discovered simultaneously in 1808, by Seebeck, at Jena, and by Berzelius and Pontin, at Stockholm, was originally prepared by the action of electricity upon aqueous ammonia in contact with mercury. A strong solution of aqueous ammonia in which mercury is placed, is brought into the voltaic circle, the negative pole dipping into the mercury, and the positive pole into the liquid. Another method is to dip the negative wire into mercury, which is placed in a cavity hollowed out of a fragment of a solid ammonium-salt, carbonate, sulphate, phosphate, or chloride, the positive wire being inserted into the salt itself, or connected with a metallic plate on which the salt rests. Oxygen, or, if chloride of ammonium be employed, chlorine, is evolved at the positive pole, but scarcely any gas at the negative pole; while the mercury increases very largely in volume, and assumes the consistence of butter. When completely saturated with ammonium, the amalgam is lighter than water: obtained by the former method, it has frequently a crystalline structure. It is a very unstable compound, decomposing spontaneously as soon as it is removed from the voltaic circle, being resolved into liquid mercury, and a mixture of 2 vols. ammonia, NH^3, and 1 vol. hydrogen, H. When cooled below 0° C., it solidifies and crystallises in cubes. At a very low temperature, it contracts, and becomes brittle; decomposition does not begin till the temperature rises to 29° C. According to Sir H. Davy, it contains 1 atom NH^4 to 753 atoms mercury. The amalgam may also be prepared without the intervention of electricity, by bringing potassium- or sodium-amalgam — the latter is more energetic in its action—into contact with an ammonium-salt, either solid and moistened with water, or as a concentrated aqueous solution. The amalgam thus prepared contains, according to Gay-Lussac and Thénard, 1 part nitrogen and hydrogen to 1800 parts mercury. It contains a certain portion of potassium or sodium, and on this account is less unstable than the amalgam prepared by either of the former methods: it may be preserved for a considerable time in anhydrous rock-oil, or in an atmosphere of hydrogen.

Formation.—Ammonium-salts are formed by bringing ammonia or carbonate of ammonium directly into contact with acids.

Properties.—Ammonium-salts are isomorphous with potassium-salts. They have mostly a pungent, saline, somewhat urinous taste. They are all soluble in water, generally with facility: less soluble in alcohol or ether. Ammonium-salts of colourless acids are colourless.

Reactions of Ammonium-salts. Tests for Ammonia.—Ammonium-salts are variously affected by heat: all, however, are wholly or partially volatilised, with or without decomposition. The carbonate, and those which contain no oxygen (chloride, iodide, &c.), are volatilised undecomposed. All others lose their ammonia when heated. Some, *e.g.* the phosphate, and borate, evolve ammonia undecomposed, leaving the acid. Others, *e.g.* sulphate, evolve nitrogen, the acid being more or less completely reduced by the hydrogen of the ammonia: the nitrate is decomposed into nitrous oxide and water. Their aqueous solution, when exposed to the air (still more rapidly when evaporated), generally loses ammonia, an acid salt, or a normal salt mixed with excess of acid, being formed: hence, in crystallising an ammonium-salt, ammonia must be occasionally added during evaporation. When treated with *chlorine*, their aqueous solution yields hydrochloric acid and nitrogen; or, if the salt contains a powerful acid, hydrochloric acid and chloride of nitrogen (Dulong). With a solution of *hypochlorous acid*, dry ammonium-salts yield water, chloride of nitrogen, and nitrogen, while nitrogen and chlorine remain in solution (Balard). In solution they are decomposed by *protoxides*, with liberation of ammonia; not by sesquioxides. When heated, either solid or in solution, with a fixed alkali, baryta, lime, oxide of lead, &c., they evolve ammonia: magnesia expels only half the ammonia, forming a double salt.

The reaction by which ammonium-salts are generally detected, is their decomposition when heated with *fixed alkalis* or *alkaline earths*. If the ammonia evolved be in so minute a quantity that its characteristic smell cannot be perceived, it is easily recognised by its property of restoring the blue colour to reddened litmus-paper, and of forming dense white fumes by contact with a glass rod moistened with dilute hydrochloric acid. If the evolved ammonia be brought into contact with a strip of paper moistened with a dilute neutral solution of subnitrate of mercury, sulphate of copper, or sulphate of manganese, in the first case a black stain is produced on the paper, in the second a blue, in the third a brown.—A solution of *molybdate of sodium containing phosphoric acid* (phosphomolybdate of sodium), gives with ammonium-salts, a yellow precipitate, soluble in alkalis and non-volatile organic acids, insoluble in mineral acids: in very dilute ammonium solutions, the formation of the precipitate is gradual; it is accelerated by heat. When a solution containing an ammonium-salt or free ammonia is mixed with potash, and a solution of *iodide of mercury in iodide of potassium* added, a brown precipitate or coloration is immediately produced (Nessler). ($NH^3 + 4HgI = NHg^4I + 3HI$). This is by far the most delicate test for ammonia.—With *dichloride of platinum*, ammonium-salts give a yellow crystalline precipitate of chloroplatinate of ammonium, $PtCl^3NH^4$, slightly soluble in water, insoluble in alcohol or acids. When ignited, the precipitate is converted into pure metallic platinum, perfectly free from chlorine. With *acid tartrate of sodium* (or *tartaric acid*), they give a white precipitate of acid tartrate of ammonium, slightly soluble in cold water, readily soluble in alkaline solutions and in mineral acids. The carbonaceous residue left on igniting this precipitate has no alkaline reaction.—A not too dilute solution of an ammonium-salt gives with a concentrated solution of *sulphate of aluminium*, a crystalline precipitate of ammonium-alum.—Only very concentrated solutions of ammonium-salts give precipitates with *perchloric* or *fluosilicic acid*.—*Subnitrate of mercury* gives a brown colour in solutions containing free ammonia.—A slightly alkaline solution of an ammonium-salt gives a white precipitate with *chloride of mercury*.—Alcoholic solutions of ammonium-salts burn with a blue or violet flame.

Reactions very similar to those just described, *e. g.* with phosphomolybdate of sodium, iodomercurate of potassium, dichloride of platinum, chloride of mercury, &c., are likewise produced by the salts of methylamine, ethylamine, and other compound ammonias. These organic bases may, however, be distinguished with certainty from ammonia itself by igniting the substance under examination with oxide of copper, and passing the evolved gases into baryta water, when, if carbon is present, a precipitate of carbonate of baryta will be produced. (See ANALYSIS, ORGANIC, p. 225.)

Separation and Estimation of Ammonium.—Ammonium is separated from all other metals except the alkaline metals, by its non-precipitation by hydrosulphuric acid, sulphide or carbonate of ammonium, or phosphate of sodium, in presence of chloride of ammonium. From sodium and lithium it is separated by dichloride of platinum and alcohol, which precipitates potassium and ammonium as chloroplatinates, while sodium and lithium remain in solution. The mixed chloroplatinates are converted by ignition into a mixture of metallic platinum and chloride of potassium, the latter of which is dissolved out by water, the solution evaporated to dryness, gently ignited, and weighed. The weight of platinum corresponding to the amount of potassium thus obtained being deducted from the total weight of metallic platinum, the remaining platinum represents the ammonium present: 1 atom of platinum corresponds to 1 atom of ammonium. This method is applicable only when the metals are present as salts which are soluble in alcohol, *e. g.* as chlorides. Sulphates are best converted into chlorides by adding carbonate of barium, and saturating the filtrate with hydrochloric acid.

The best method for the separation of ammonium from all other metals is to heat the compound under examination in a combustion-tube with excess of soda-lime, and to collect the ammonia evolved in a bulb-apparatus containing hydrochloric acid. The chloride of ammonium thus obtained is mixed with excess of dichloride of platinum (perfectly free from nitric acid), and evaporated to dryness on a water-bath. The residue is treated with alcohol, which dissolves excess of the dichloride: the chloroplatinate of ammonium is collected on a weighed filter, dried at 100° C., and weighed; or converted by ignition in a porcelain crucible into metallic platinum, from the weight of which the amount of ammonia is readily calculated. This method is not applicable to the separation of ammonia from other volatile organic bases.

Ammonium-salts may occasionally be estimated by loss. This is the case when the ammonium-salt is entirely volatile, and when no other volatile or decomposible compound is present. The substance under examination is heated in a water-bath until it ceases to lose weight: it is then moderately ignited and weighed again, when the loss of weight represents the amount of ammonium-salt present. This is a convenient method for the estimation of chloride, nitrate, or normal sulphate of ammonium, in presence of the corresponding fixed alkaline salts.

Ammonia may also be estimated by distilling it into a known quantity of dilute acid, and determining volumetrically by a standard alkaline solution the excess of free acid.

The following are the principal ammonium-salts:

1. ACETATES OF AMMONIUM. *a. Normal acetate*, $C^2H^3O^2.NH^4$.—A white odourless salt, obtained by saturating glacial acetic acid with dry ammonia.

b. Acid acetate, $C^2H^3O^2.NH^4 + C^2H^4O^2$.—Obtained as a white crystalline sublimate, when dry powdered chloride of ammonium is treated with an equal weight of acetate of potassium or calcium, ammonia being given off simultaneously. (See ACETATES, p. 12.)

2. CARBONATES OF AMMONIUM.—H. Rose (Pogg. Ann. xlviii. 352) admits the existence of a considerable number of carbonates of ammonium, to which he assigns very various and complicated formulæ. But, according to H. Deville (Compt. rend. xxxiv. 880; Ann. Ch. Phys. [3] xl. 87), there exist only two carbonates of ammonium of definite composition.

a. Normal carbonate, $CO^3(NH^4)^2$ [or $CO^2.NH^4O = CO^2.NH^3.HO$].—This salt has never been isolated. The salt which crystallises from an alcoholic solution of sesquicarbonate of ammonium saturated with ammonia, is simply sesquicarbonate. Neither can it be obtained from a saturated solution of commercial sesquicarbonate in strong aqueous ammonia. It may be obtained in aqueous or alcoholic solution, or, as sesquicarbonate, in combination with the acid carbonate (*b*). (Pelouze et Fremy, Traité de Chimie, ii. 222.)

b. Acid carbonate, $CO^3.NH^4.H$ [or $CO^2.NH^4O + CO^2.HO$.]—Obtained by saturating an aqueous solution of ammonia or sesquicarbonate of ammonium with carbonic anhydride. Or by treating the commercial sesquicarbonate finely powdered, with alcohol of 90 per cent., which dissolves out normal carbonate, leaving a residue of acid carbonate. Sesquicarbonate of ammonium is similarly decomposed by cold water; but in this case, a larger quantity of the acid carbonate is dissolved. All carbonates of ammonium, when left to themselves, are gradually converted into acid carbonate. It forms large crystals, belonging to the right prismatic or trimetric system. According to Deville, it is dimorphous, but never isomorphous with acid carbonate of potassium. When exposed to the air, it volatilises slowly, without becoming opaque, and gives off a slight ammoniacal odour. At the ordinary temperature, it is soluble in 8 parts of water; if this solution be heated above 36° C. it is decomposed, evolving carbonic anhydride. Even at ordinary temperatures, the solution, whether concentrated or dilute, gradually becomes ammoniacal on keeping (Gmelin). It is insoluble in alcohol; but when exposed to the air under alcohol, it dissolves as normal carbonate, evolving carbonic anhydride.

It has been found native in considerable quantity in the deposits of guano on the western coast of Patagonia, in the form of white crystalline masses, with a strong ammoniacal smell. (Ulex. Ann. Ch. Pharm. lxvi. 44.)

c. Sesquicarbonate, $C^3O^9N^4H^{16} + 2H^2O$ [$= 3CO^2.2NH^4O + 3HO$.]—Obtained by dissolving commercial carbonate of ammonium in strong aqueous ammonia, at about 30° C., and crystallising the solution. It forms large transparent crystals, representing a right rectangular prism, with the faces of the corresponding rhombic octahedron resting on the angles. These crystals decompose very rapidly in the air, losing water and ammonia, and being converted into di-acid carbonate. This salt may be regarded as a mixture or compound of 1 atom of normal carbonate with 2 of atoms acid carbonate [$CO^3.(NH^4)^2 + 2(CO^3.NH^4.H) = C^3O^9N^4H^{16}$]: a view which is confirmed by its behaviour with water and alcohol; which, when added in quantity insufficient for the complete solution of the salt, dissolves out normal carbonate, leaving a residue of acid carbonate: 100 pts. water at 13° C. dissolve 25 pts. sesquicarbonate, at 17°, 30 pts.; at 32°, 37 pts.; at 41°, 40 pts.; at 49°, 50 pts. (Berzelius): above this temperature, carbonic anhydride is evolved, and a solution of normal carbonate formed.

Commercial carbonate of ammonium (*sal volatile, salt of hartshorn*, &c.) consists of sesquicarbonate, more or less pure. It is prepared on a large scale by the dry distillation of bones, hartshorn, and other animal matter. The product thus obtained is contaminated with empyreumatic oil, from which it is purified by subliming it once or twice with 1½ times its weight of animal charcoal, in cast-iron vessels over which glass receivers are inverted. By repeated sublimation, the salt is partially decomposed. Another method of preparing it is by heating to redness a mixture of 1 pt. chloride or sulphate of ammonium, and 2 pts. carbonate of calcium (chalk), or carbonate of potassium, in a retort to which a receiver is luted: ammonia and water are first disengaged, and then the sesquicarbonate distils over and solidifies in the neck of the retort and the receiver. On a small scale, glass vessels are employed: on a large scale, an earthenware or cast-iron retort, and an earthenware or leaden receiver, which, when filled by repeated distillations, is broken or cut in two: 10 pts. sal-ammoniac yield from 7 to 8 pts. sesquicarbonate. (See *Dictionary of Arts, Manufactures and Mines*, i. 135.) The salt thus prepared is liable to contain the following impurities:

Hyposulphite of ammonium: when sulphate of ammonium, or chloride containing sulphate, is employed in the preparation. The salt neutralised with acetic acid gives a white precipitate which turns black on addition of nitrate of silver.—*Sulphate of ammonium*, from the same causes: detected by hydrochloric acid and chloride of barium. —*Sal-ammoniac:* detected by nitric acid and nitrate of silver.—*Lead*, from the receiver: the salt has a grey colour, and when dissolved in dilute nitric acid, gives the reactions of lead.—*Lime* and *chloride of calcium*, carried over mechanically: from these and other fixed impurities the salt is freed by re-sublimation.

The sesquicarbonate obtained as above is a white, transparent, fibrous mass, with a pungent caustic taste, and a strong ammoniacal smell. Exposed to the air, it is gradually converted into acid carbonate. It is completely volatile, though not without partial decomposition. Its aqueous solution is strongly alkaline: from a hot saturated solution, the acid carbonate crystallises on cooling, but not in the ordinary crystalline form. (Deville.)

The aqueous solution of this salt (*spiritus salis ammoniaci*), is extensively employed in medicine as a stimulant. It is also a very valuable reagent. The solid salt is employed in the manufacture of other ammoniacal salts.

3. CHLORIDE OF AMMONIUM, $ClNH^4$. (*Hydrochlorate* or *muriate of ammonia*, *Sal-ammoniac*, *salzsaures Ammoniak*, *Salmiak*, *Chlorure d'ammonium*, or *Chlorure ammonique*.)

Hydrochloric acid gas and ammonia combine volume for volume, with great evolution of heat, forming solid chloride of ammonium. This salt forms colourless feathery crystals, which, when examined by a lens, are found to consist of an aggregation of cubes or octahedrons. It has no smell, but a pungent taste; its specific gravity is 1·5. It dissolves in 2·72 pts. water at 18·75° C., with great reduction of temperature; and in about its own weight of water at 100°. It is less soluble in alcohol. When exposed to the air, it loses ammonia, and becomes acid to test-paper. When heated, it volatilises undecomposed, without previous fusion. After sublimation, it forms white crystalline masses, which are exceedingly tough and difficult to powder: to obtain it in a pulverulent state, a hot saturated solution is evaporated to dryness very rapidly, with continual agitation, when the salt is left as a crystalline powder.

Chloride of ammonium is decomposed by several metals, potassium, iron, &c., a metallic chloride being formed, and ammonia and hydrogen separated. It is also decomposed by many salts; by some, *e. g.* alkaline and alkaline-earthy hydrates, completely, ammonia being evolved; by others, as by cupric and ferric salts, partially, double salts being formed. Some salts, *e. g.* platinic chloride, combine with it directly, forming double salts (chloroplatinates). Some metallic hydrates are soluble in a solution of sal-ammoniac, especially those of zinc and magnesium.

Sal-ammoniac is found native in many volcanic regions; also in small quantities in sea-water. It is readily formed by heating nitrogenised animal matter containing chloride of sodium, or with which that salt has been mixed. Until the middle of the last century, sal-ammoniac was obtained almost exclusively from Egypt, where it was prepared in this manner, by subliming the soot obtained by the combustion of camel's dung. It is now largely manufactured in Europe, chiefly from the impure carbonate of ammonium which is obtained in gas-works, or by the dry distillation of animal matter. This carbonate is converted into chloride by the addition of hydrochloric acid, or of the mother-liquor from salt-works, containing the chlorides of magnesium and calcium, and by evaporating the solution (ammonia being added from time to time), crystals of sal-ammoniac are obtained. These are contaminated with empyreumatic oil, which is destroyed by heating the crystals to a temperature a little below their subliming point. They are then dissolved in water, the solution decolorised by boiling with animal charcoal, and again crystallised. The salt is finally purified by sublimation, which is performed at a brisk heat, in large glass or earthenware bottles, the neck of which must be carefully kept unobstructed, to avoid the risk of explosion: the bottles are then broken and the sal-ammoniac removed in cakes. Metallic receivers are sometimes employed in the sublimation; in this case, the outer surface of the sal-ammoniac is dark-coloured, owing to metallic impurities, and must be scraped off.

In some manufactories, the carbonate of ammonium is first converted into sulphate, and subsequently into chloride. This is generally done by filtering the solution of carbonate through a stratum of powdered gypsum (sulphate of calcium), when insoluble carbonate of calcium is formed, and a solution of sulphate of ammonium obtained. This solution is mixed with chloride of sodium, evaporated to dryness, and the sal-ammoniac separated from the residue by sublimation. Or the solution of the two salts is evaporated at the boiling heat, when sulphate of sodium, being less soluble at a high than at a lower temperature, mostly crystallises out and is removed. The solution is then cooled, when the sal-ammoniac crystallises out, since its solubility diminishes rapidly with decrease of temperature. The crystals thus obtained are purified as above described. Ferrous sulphate may be employed instead of gypsum to convert the carbonate of ammonium into sulphate; this is a more expensive process, but it possesses the advantage of removing the greater part of the empyreumatic oil, which is carried down by the precipitated iron-salt. (Berzelius.)

In the factory at Buxweiler, in Alsace, sal-ammoniac, phosphorus, and gelatin are prepared by the following ingenious process. Bones are digested in hydrochloric acid, which dissolves out the bone-earth, leaving the cartilage insoluble: the latter is employed for the preparation of gelatin. The hydrochloric solution is mixed with crude carbonate of ammonium, when sal-ammoniac is formed, and phosphate of calcium precipitated in the finely-divided state in which it is best adapted for the preparation of phosphorus. [For further details of the manufacture of sal-ammoniac, see *Dictionary of Arts, Manufactures and Mines*, i. 141.]

Sal-ammoniac is employed in medicine. In the laboratory it serves for the preparation of ammonia, and carbonate of ammonium, and for frigorific mixtures. It is employed in dyeing; also in metal-works, as a deoxidising agent, especially for copper. A solution of chloride of silver in chloride of ammonium is employed for plating copper and brass. It enters into the composition of a cement used for fixing iron in stone: this cement is formed by moistening with a solution of sal-ammoniac, iron-filings mixed with 1 or 2 per cent. sulphur. Impure sal-ammoniac has recently been employed as manure.

4. HYDRATE OF AMMONIUM, $NH^4.H.O.$—This compound has never been isolated. The aqueous solution of ammonia behaves in many respects like a solution of hydrate of ammonium.

5. NITRATE OF AMMONIUM, $NO^3.NH^4$ [or $NO^5.NH^4O = NO^5.NH^3.HO$]. (*Nitrum flammans.*)—Obtained by crystallising a mixture of nitric acid with a slight excess of aqueous ammonia. It forms long flexible needles: if the crystallisation be effected very slowly, it may be obtained in six-sided prisms. When the solution is evaporated to a very small bulk, the salt solidifies into a dense amorphous mass. It has a pungent taste. It is soluble in about half its weight of water at 18° C., and in still less at 100°: its saturated solution boils at 164° C., and contains 47·8 per cent. salt: when dissolved in water it produces great cold. It is soluble in alcohol. Exposed to the air, it deliquesces slightly, loses ammonia, and becomes acid. When heated, it fuses perfectly at 108° C., and boils without decomposition at 180°. Between 230° and 250° it is decomposed into water and nitrous oxide, ($NO^3.NH^4 = N^2O + 2H^2O$). If it be heated too rapidly, ammonia, nitric oxide, and nitrite of ammonium are also formed. (Berzelius). When thrown into a red-hot crucible, it burns with a slight noise, and a pale yellow flame. In presence of spongy platinum, it is decomposed at about 170° C. into nitrogen and nitric acid. (Millon and Reiset.)

Nitrate of ammonium is formed when a mixture of nitrogen, oxygen, and excess of hydrogen is submitted to the electric current; also when hydrosulphuric acid is passed into a dilute solution of nitric acid. It is also formed by the action of nitric acid on several metals, especially tin.

6. NITRITE OF AMMONIUM, $NO^2.NH^4$ [$= NO^3.NH^3.HO$].—Obtained by double decomposition of nitrite of lead and sulphate of ammonium, or of nitrite of silver and chloride of ammonium: the solution is evaporated in vacuo. Or by passing nitrous fumes into aqueous ammonia, and evaporating over lime (Millon). It forms an imperfectly crystallised mass. It is decomposed by heat into nitrogen and water, ($NO^2.NH^4 = N^2 + 2H^2O$). Its aqueous solution is similarly decomposed, suddenly if acid, gradually if alkaline.

7. OXALATES OF AMMONIUM. —*a. Normal oxalate.* $C^2O^4(NH^4)^2 + H^2O$.—Obtained by neutralising oxalic acid with ammonia, and crystallising. It forms long prisms united in tufts, belonging to the rhombic, right prismatic or trimetric system: soluble in 3 pts. cold water, insoluble in alcohol. It is very slightly volatile at ordinary temperatures. When carefully heated to 220° C. it is entirely decomposed into carbonic oxide and carbonate of ammonium; when it is heated more strongly, some oxamide is formed. Its solution is employed as a reagent for precipitating calcium-salts.

b. Acid oxalate, $C^2O^4.NH^4.H + H^2O$. — Obtained in the crystalline form by adding oxalic, sulphuric, nitric, or hydrochloric acid to a solution of the normal salt. It crystallises in the trimetric system. It reddens litmus, and is less soluble than the normal salt. It is decomposed by heat, yielding, among other products, oxamide, $\mathrm{C^2O^2N^2H^4}$, and oxamic acid, $\mathrm{C^2O^3NH^3}$.

c. Quadroxalate, Hyper-acid oxalate, $\mathrm{C^2O^4.NH^4.H + C^2O^4H^2 + 2H^2O}$. — Obtained by crystallising a solution of equal parts of acid oxalate and oxalic acid. The crystals belong to the triclinic or doubly oblique prismatic system, and are isomorphous with the corresponding potassium salt. They are very soluble in hot water. At 100° C. they effloresce slightly, and lose their water of crystallisation.

8. PHOSPHATES OF AMMONIUM. — *a. Normal phosphate*, $\mathrm{PO^4(NH^4)^3}$ [or $PO^5.3NH^4O.$] —When a solution of monacid phosphate of ammonium is mixed with ammonia, this salt separates as a crystalline magma: it cannot be dried without losing ammonia, being converted into *b*.

b. Diammonic phosphate, $\mathrm{PO^4.(NH^4)^2.H}$ [or $PO^5.2NH^4O.HO$]. (*Ordinary phosphate of ammonium*, formerly called *neutral phosphate.*)—Obtained by adding a slight excess of ammonia or carbonate of ammonium to acid phosphate of calcium (solution of bone-earth in hydrochloric or dilute sulphuric acid); when phosphate of calcium is precipitated, and monacid phosphate of ammonium remains in solution. It forms large, colourless, transparent crystals, belonging to the monoclinic or oblique prismatic system. It has a cooling, saline taste, and an alkaline reaction. Exposed to the air, it effloresces slightly, losing ammonia. It is soluble in 4 pts. cold, and in a smaller quantity of boiling water; insoluble in alcohol. By a red heat, it is converted into metaphosphoric acid, $\mathrm{PO^4.(NH^4)^2.H = PO^3H + 2NH^3 + H^2O}$).

c. Monammonic phosphate, $\mathrm{PO^4.(NH^4).H^2}$ [or $PO^5.NH^4O.2HO$]. (Formerly called *acid phosphate.*) — Obtained by adding phosphoric acid to aqueous ammonia, till the solution is strongly acid, and no longer precipitates chloride of barium; or by boiling a dilute solution of *b* and evaporating it to crystallisation. It crystallises in the dimetric or square prismatic system. It is somewhat less soluble in water than *b*, and is similarly decomposed by heat.

The phosphates of ammonium are employed for the preparation of metaphosphoric acid. As the residue of their ignition always retains ammonia, it must be moistened with nitric acid, and again calcined. Gay-Lussac has proposed to preserve muslins and other inflammable textures from ignition by steeping them in a solution of these salts; the salt being decomposed by heat, the tissue is covered with a film of metaphosphoric acid, which preserves it from contact with the air, and prevents its breaking into flame. These salts cannot, however, be applied to fabrics which have to be washed and ironed, because the heat of the iron would decompose them, expelling the ammonia. The same objection applies to sulphate of ammonium, which is otherwise efficacious in diminishing the inflammability of light tissues. From recent experiments by Versmann and Oppenheim (Pharm. J. Trans. [2] i. 385), it appears that the only salt universally applicable for rendering such fabrics non-inflammable, is the neutral tungstate of sodium. (See TUNGSTATES.)

Some of the double phosphates of ammonium and other metals are of considerable importance. The phosphate of sodium, ammonium and hydrogen, $\mathrm{PO^4.Na.NH^4.H}$, commonly called *microcosmic salt*, or *phosphorus salt*, is much used as a blow-pipe flux, being converted by heat into transparent metaphosphate of sodium, which dissolves many metallic salts with characteristic colours.

9. SULPHATES OF AMMONIUM. — *a. Normal Sulphate*, $\mathrm{SO^4(NH^4)^2}$ [or $SO^3.NH^4O.$] (Glauber's *Sel secretum.*) — Obtained by neutralising dilute sulphuric acid with ammonia or carbonate of ammonium. It forms crystals belonging to the trimetric or right prismatic system, isomorphous with potassic sulphate. It is colourless, and has a very bitter taste; it is soluble in twice its weight of cold, and in its own weight of boiling water; insoluble in alcohol. It fuses at 140° C: above 280°, it is decomposed, ammonia, nitrogen, and water being given off, and acid sulphite of ammonium sublimed.

It is found native as *Mascagnine*. It is manufactured on a large scale (as already described under Sal-ammoniac) by neutralising with sulphuric acid, or decomposing by gypsum, the impure carbonate of ammonium obtained in gas-works, &c. and crystallising the solution. The crystals are heated, to destroy animal matter, and purified by recrystallisation. Sulphate of ammonium is employed in the manufacture of ammonium-alum: also as manure.

b. Acid sulphate, $\mathrm{SO^4.NH^4.H}$, [or $2SO^3.NH^4O.HO$].—Obtained by treating a solution of *a* with sulphuric acid. It crystallises in thin rhombohedrons. It is soluble in its own weight of cold water, and in alcohol. It deliquesces slowly in the air.

10. SULPHIDES OF AMMONIUM.—*a. Sulphide*, $\mathrm{(NH^4)^2S}$.—When a mixture of dry hydrosulphuric acid and ammonia, the latter in excess, is exposed to a temperature of − 18° C. 2 vols. ammonia combine with 1 vol. hydrosulphuric acid, and form sulphide of ammonium. The same compound is formed when sulphide of potassium is distilled

with chloride of ammonium, provided the receiver be cooled to −18° C. It forms colourless crystals, which have a strong alkaline reaction. At the ordinary temperature, it is at once decomposed, losing ammonia, and being converted into sulphydrate (*b*). This decomposition takes place even in an atmosphere of ammonia. Its aqueous solution, which is much employed as a reagent, is prepared by dividing a saturated solution of ammonia into 2 equal parts, saturating one with hydrosulphuric acid, and then adding the other. It forms a colourless solution, which becomes yellow on keeping, owing to the formation of a higher sulphide; by further exposure to the air, sulphur is separated, hyposulphite, sulphite, and finally sulphate of ammonium being successively formed.

b. Sulphydrate or *Hydrosulphate*, $NH^4.H.S.$—Obtained by mixing dry hydrosulphuric acid and ammonia, in any proportions, at a temperature above −18° C. It is a combination of the two gases in equal volumes. It forms colourless crystals, which have an alkaline reaction, and volatilise undecomposed, even at ordinary temperatures. Its aqueous solution is obtained by saturating aqueous ammonia with washed hydrosulphuric acid, out of contact with the air. It forms a colourless solution, which, by exposure to the air, is decomposed in the same manner as the sulphide.

c. Polysulphides.—Besides the above, there are several other compounds of sulphur and ammonium described, which may be regarded as combinations of the monosulphide with sulphur, or as polysulphides of ammonium. These are—1. The *disulphide*, $(NH^4)^2S^2$; 2. The *trisulphide*, $(NH^4)^2S^3$; 3. The *tetrasulphide*, $(NH^4)^2S^4$; 4. The *pentasulphide*, $(NH^4)^2S^5$; 5. The *heptasulphide*, $(NH^4)^2S^7$. The most general method of preparing these compounds is by distilling the corresponding sulphide of potassium with excess of chloride of ammonium. In the wet way, they are prepared by adding sulphur to a solution of the monosulphide, and saturating the mixture alternately with ammonia and hydrosulphuric acid. The heptasulphide, to which there is no corresponding sulphide of potassium, is formed by the spontaneous decomposition of the pentasulphide:

$$3(NH^4)^2S^5 = 2(NH^4)^2S^7 + NH^3 + NH^4.H.S.$$

It forms ruby-red crystals. It is the most stable of the polysulphides of ammonium, not being decomposed at temperatures below 300° C., and but very slowly by water or hydrochloric acid.

The substance known as *fuming liquor of Boyle*, or *volatile liver of sulphur*, is a mixture of two or more sulphides of ammonium. It is obtained by distilling a mixture of 1 pt. sulphur, 2 pts. sal-ammoniac, and 2 to 3 pts. quick lime. It is a dark yellow liquid, of penetrating smell: it fumes strongly in the air, or in any gas containing oxygen, not in gases free from oxygen. It is capable of taking up more sulphur, forming a syrupy fluid, which no longer fumes on contact with air.—F. T. C.

AMMONIUM. A hypothetical metal, whose composition is expressed by the formula NH^4: it is supposed to be contained in ammoniacal salts. (See AMMONIACAL SALTS, p. 188.)

AMMONIUM-AMALGAM. (p. 188.)

AMMONIUM-BASES. In very many cases, the watery solution of ammonia behaves with other bodies exactly like a solution of potash or soda. We cannot express this similarity in our chemical formulæ, if we regard liquid ammonia as a mere solution of ammonia, NH^3, in water: it only becomes comparable to the fixed alkalis when we regard it as containing a compound of ammonia with water, $NH^3.H^2O$. In order to express this relation still more precisely, Berzelius proposed to represent aqueous ammonia as containing the hydrated oxide of the compound group, NH^4,—($NH^3.H^2O = \left.\begin{matrix}NH^4\\H\end{matrix}\right\}O$), to which he gave the name *Ammonium*, and by means of which the ammonia-salts can be represented as exactly analogous to those of potassium, sodium, or the metals generally (see AMMONIUM-SALTS, p. 188). In the article AMIDES, it is shown that a very large number of bodies may be formed from ammonia, by replacing a part or the whole of its hydrogen by other radicles, simple or compound. When the hydrogen of ammonia is replaced by the alcohol-radicles (methyl, ethyl, &c.), or by other bodies which more or less resemble hydrogen in their general chemical characters, the resulting compounds (*Amines*) retain the most important property of ammonia itself, namely, the property of forming definite salts by direct union with acids. It is evident that, if it is wished to express the analogy of the salts of these derivatives of ammonia with the metallic salts, they may be represented as containing ammonium in which part of the hydrogen is replaced by other radicles: for instance, hydrochlorate of triethylamine, $NC^6H^{16}Cl$, may be viewed as chloride of triethylammonium, $[N(C^2H^5)^3H]Cl$, analogous to chloride of ammonium, $(NH^4)Cl$, and chloride of potassium, KCl.

But since only three-fourths of the hydrogen of the ammonium in ammonia-salts is derived from ammonia, the other fourth belonging to the acid, it is plain that the compounds of the derived ammonias with acids never represent ammonium-salts in which more than three-fourths of the hydrogen is replaced. But, by the combination of tertiary amines (derivatives of ammonia by the replacement of all three atoms of hydrogen by methyl, ethyl, or similar radicles), with the chlorides, bromides, or iodides of the alcohol-radicles, compounds are formed which represent ammonium-salts in which all the hydrogen is replaced by other radicles (see Amides, p. 175): *e. g.*

$$\underset{\text{Triethylamine.}}{N.(C^2H^5)^3} + \underset{\substack{\text{Iodide of}\\\text{ethyl.}}}{C^2H^5.I} = \underset{\substack{\text{Iodide of}\\\text{tetrethylium.}}}{N.(C^2H^5)^4I}$$

Notwithstanding the obvious analogy of this mode of formation to the formation of the salts of amines by the action of the iodides, &c, of alcohol-radicles on ammonia — *e. g.*:

$$NH^3 + \underset{\substack{\text{Iodide of}\\\text{ethyl.}}}{C^2H^5I} = \underset{\substack{\text{Hydriodate of}\\\text{ethylamine.}}}{N.(C^2H^5.H^3)I};$$

the seriation which connects this class of bodies with the ammonium-salts: —

$N.H \;.\; H \;.\; H \;.\; H \;.\; I,$	hydriodate of ammonia, or iodide of ammonium,
$N.C^2H^5 \;.\; H \;.\; H \;.\; H \;.\; I,$	„ ethylamine, „ ethylium,
$N.C^2H^5 \;.\; C^2H^5 \;.\; H \;.\; H \;.\; I,$	„ diethylamine „ diethylium,
$N.C^2H^5 \;.\; C^2H^5 \;.\; C^2H^5 \;.\; H \;.\; I,$	„ triethylamine „ triethylium,
$N.C^2H^5 \;.\; C^2H^5 \;.\; C^2H^5 \;.\; C^2H^5 \;.\; I,$	iodide of tetrethylium;

and the applicability of the ammonium-theory to express the nature of the salts of the amines, as pointed out above — the derivatives of the ammonium-salts by the replacement of all the hydrogen of the ammonium, nevertheless exhibit some important general differences from the salts of the amines. For example, when caustic potash or lime is added to a salt of ammonia, or of an amine, the salt is decomposed, even in the cold, and ammonia, or a derivative, is set at liberty; on the other hand, iodide of tetrethylium, or a similar compound, is not decomposed by potash; it can however be decomposed by hydrate of silver; but, even then, there is no separation of a derivative of ammonia, but hydrate of tetrethylium, $N.(C^2H^5)^4.H.O$, or a similar body, is formed:

$$\underset{\substack{\text{Iodide of}\\\text{tetrethylium.}}}{N(C^2H^5)^4I} + AgHO = \underset{\substack{\text{Hydrate of}\\\text{tetrethylium.}}}{N(C^2H^5)^4.H.O} + AgI.$$

In the first case, the hydrate of ammonium, which may be supposed to be formed in the first stage of the reaction, is decomposed into ammonia and water: in the second case, the substance which represents hydrate of ammonium is stable and has the properties of a strong alkali. This difference makes it convenient to have some general term to distinguish such bodies as hydrate of tetrethylium from such basic hydrates as decompose, at the moment of their formation, into a representative of ammonia and water. The former class of substances are therefore often spoken of as *ammonium-bases*, in contradistinction to the *amine-* or *ammonia-bases.*

The formation of the ammonium-bases is specially interesting in connection with the theory of ammonium. It is impossible to isolate the hydrate of ammonium, which, according to that theory, exists in solution of ammonia, or to obtain a corresponding compound from any of the compound ammonias; but the ammonium-bases are representatives of hydrate of ammonium, which correspond to the hydrates of potassium and sodium, not only in their formulæ, but very closely in their properties. Their concentrated solution is caustic to the touch; by evaporation, they are obtained as crystalline substances, very soluble in water, which liberate ammonia from its salts, dissolve most of the metallic oxides which are soluble in potash, and decompose compound ethers into the corresponding acid and alcohol. At a high temperature, they are decomposed, with formation of a tertiary amine:

$$\underset{\substack{\text{Hydrate of}\\\text{tetrethylium.}}}{N.(C^2H^5)^4.H.O} = \underset{\substack{\text{Triethyl-}\\\text{amine.}}}{N.(C^2H^5)^3} + \underset{\substack{\text{Ethy-}\\\text{lene.}}}{C^2H^4} + H^2O.$$

Their iodides, or similar salts, are similarly decomposed by heat:

$$\underset{\substack{\text{Iodide of}\\\text{tetrethylium.}}}{N(C^2H^5)^4I} = \underset{\substack{\text{Triethyl-}\\\text{amine.}}}{N(C^2H^5)^3} + \underset{\substack{\text{Iodide}\\\text{of ethyl.}}}{C^2H^5.I.}$$

The tertiary derivatives of phosphide, arsenide, and antimonide of hydrogen, give rise to precisely similar compounds by combination with hydriodic ethers and subsequent decomposition of the iodide so formed, by hydrate of silver. The decomposition by heat of the hydrates of the *phosphonium-bases*, differs from that of the corresponding ammonium-bases: *e. g.*

$$\underset{\substack{\text{Hydrate of}\\ \text{tetrethyl-}\\ \text{phosphonium.}}}{P(C^2H^5)^4H.O} = \underset{\substack{\text{Oxide of}\\ \text{triethylphos-}\\ \text{phine.}}}{P(C^2H^5)^3O} + \underset{\substack{\text{Hydride of}\\ \text{ethyl.}}}{C^2H^5.H.}$$

POLYAMMONIUM-BASES.—These compounds bear to the monammonium-bases just described, the same relation that the diamines and triamines bear to the monamines: they may be considered as representing two or more molecules of hydrate of ammonium in which the whole or part of the hydrogen is replaced by polyatomic radicles. As in the case of the monammonium-bases, there is a difference between the polyammonium-bases in which only part of the hydrogen is replaced, and those in which it is all replaced: the former cannot be obtained in the isolated state; the latter are stable compounds and possess strong alkaline properties. But both these classes of hydrates have been less studied, and are therefore hitherto less important, than the corresponding salts, which are for the most part equally stable, whether still containing replaceable hydrogen, or no. We shall therefore in this article treat of the polyammonium compounds generally, making no essential distinction between hydrates and other salts, or between those compounds in which the hydrogen of ammonium is wholly, and those in which it is partially replaced. Moreover, as the bodies of this class containing phosphorus and arsenic have been at least as much studied as those containing nitrogen, it will be most convenient to speak of the action of polyatomic compounds on the basic derivatives of ammonia generally, taking as special examples of the various reactions hitherto known, compounds containing nitrogen, phosphorus, or arsenic, as these or those happen to be best known.

A. ACTION OF DIATOMIC CHLORIDES, BROMIDES, OR IODIDES: —

1. *On Ammonia.*

The experiments which have been made in this direction are almost confined to the action of bromide of ethylene on ammonia. The products thus formed are the following:

Dibromide of ethylene-diammoniuum . . .	$N^2(\overset{\prime\prime}{C}{}^2H^4)H^6Br^2$
Dibromide of diethylene-diammonium . . .	$N^2(\overset{\prime\prime}{C}{}^2H^4)^2H^4Br^2$
Dibromide of triethylene-diammonium . . .	$N^2(\overset{\prime\prime}{C}{}^2H^4)^3H^2Br^2$.

These compounds, when distilled with potash, give, respectively, ethylenamine, $N^2(\overset{\prime\prime}{C}{}^2H^4)H^4$, diethylenamine, $N^2(\overset{\prime\prime}{C}{}^2H^4)^2H^2$, and triethylenamine, $N^2(\overset{\prime\prime}{C}{}^2H^4)^3$, bodies which are likewise acted on by bromide of ethylene, the final product being a substance very analogous to bromide of tetrethylium, and which is probably dibromide of tetrethylene-diammonium, $N^2(\overset{\prime\prime}{C}{}^2H^4)^4Br^2$.

2. *On Primary derivatives of ammonia, primary amines.*

Bromide of ethylene gives with ethylamine and phenylamine:

Dibromide of ethylene-diethyl-diammonium . .	$N^2(\overset{\prime\prime}{C}{}^2H^4)(C^2H^5)^2H^4Br^2$
Dibromide of diethylene-diethyl-diammonium .	$N^2(\overset{\prime\prime}{C}{}^2H^4)^2(C^2H^5)^2H^2Br^2$.

and similar phenyl-compounds.

3. *On Tertiary derivatives of ammonia.*

Just as dibasic acids can combine with one or with two atoms of ammonia, so likewise can diatomic ethers (such as chloride or bromide of ethylene, or iodide of methylene) combine with one or with two atoms of the tertiary derivatives of ammonia.[*] Thus triethylphosphine with bromide of ethylene gives the compounds —

$\left.\begin{array}{r}(C^2H^4)''Br^2\\ (C^2H^5)^3P\end{array}\right\}$	"Bromide of bromethyl-triethylphosphonium" (Hofmann).
$\left.\begin{array}{r}(C^2H^4)''Br^2\\ 2[(C^2H^5)^3P]\end{array}\right\}$	"Bromide of ethylene-hexethyl-diphosphonium" (Hofmann).

The condition of the bromine contained in these compounds is worth noticing. The addition of nitrate of silver to a solution of the first compound precipitates only half the bromine contained in it, but nitrate of silver precipitates all the bromine contained in the second. This difference is explained by Hofmann, by supposing that 1 atom of

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[*] Bromide of ethylene and iodide of methylene combine directly with only 1 atom of the tertiary amines, but the compounds with two atoms can be obtained by the action of hydrobromic, or hydriodic ethers on ethylenamine.

bromine in the first compound is contained in the form of *bromethyl*, C^2H^4Br: his view of the constitution of the two compounds is expressed in the names quoted above. It is not, however, difficult to account for the difference in the behaviour of the two bromides without making this supposition. When we remember that the bromine in bromide of ethyl is not precipitated by nitrate of silver, but that it becomes so immediately bromide of ethyl is combined with ammonia or an analogous body, it does not seem surprising that *one* of the two atoms of bromine in bromide of ethylene should become saline (or accessible to ordinary reagents) when that body is combined with *one* molecule of a representative of ammonia, and that *both* atoms should become saline when it is combined with two molecules of an ammonia-derivative. In all compounds formed upon the model of the first compound, only 1 atom of the salt-radicle is precipitable by nitrate of silver; in all those formed upon the model of the second, both atoms are precipitable.

The following are the most important transformations of the above or similar bodies.

a. The compound $\left.\begin{matrix}C^2H^4Br^2 \\ (C^2H^5)^3P\end{matrix}\right\}$ is decomposed by heat thus:—

$$\left.\begin{matrix}C^2H^4Br^2 \\ (C^2H^5)^3P\end{matrix}\right\} = HBr + \underset{\text{Bromide of vinyl-triethylphosphonium.}}{\left.\begin{matrix}C^2H^3Br \\ (C^2H^5)^3P\end{matrix}\right\}}$$

b. When a dilute solution is treated with hydrate of silver, it loses all its bromine and gives $\left.\begin{matrix}(C^2H^4)''H^2.O^2 \\ (C^2H^5)^3P\end{matrix}\right\}$, which may be regarded as a compound of triethylphosphine with glycol. This substance is a strong base, but, as in the bromine compound, only one half of the elements combined with the ethylene, are directly replaceable by acid radicles (*e. g.* hydrochloric acid gives $\left.\begin{matrix}C^2H^4.HO.Cl \\ (C^2H^5)^3P\end{matrix}\right\}$): with bromide of phosphorus, it regenerates the original bromine-compound. In a concentrated solution, hydrate of silver gives $\left.\begin{matrix}(C^2H^4)''O \\ (C^2H^5)^3P\end{matrix}\right\}$, differing from the last substance by the elements of an atom of water. This compound may be regarded as containing oxide of ethylene and triethylphosphine, and belongs to the same class of bodies as the bases * which Wurtz obtained by the action of ammonia on oxide of ethylene:—

$$\underset{\text{Ethylene-triethylhydorphosphine.}}{\left.\begin{matrix}C^2H^4.O \\ (C^2H^5)^3P\end{matrix}\right\}} \qquad \underset{\text{Diethylene-dihydoramine.}}{\left.\begin{matrix}2(C^2H^4.O) \\ H^3N\end{matrix}\right\}} \qquad \underset{\text{Triethylene-trihydoramine.}}{\left.\begin{matrix}3(C^2H^4.O) \\ H^3N\end{matrix}\right\}}$$

c. The same compound is converted by acetate of silver at 100° C. into acetate of vinyl-triethylphosphonium, $P(C^2H^5)^3C^2H^3.C^2H^3O^2$. This reaction probably has two stages:—

$$1^\circ \quad \left.\begin{matrix}C^2H^4.Br^2 \\ (C^2H^5)^3P\end{matrix}\right\} + 2(C^2H^3AgO^2) = \left.\begin{matrix}C^2H^4.(C^2H^3O^2)^2 \\ (C^2H^5)^3P\end{matrix}\right\} + 2AgBr$$

$$2^\circ \quad \left.\begin{matrix}C^2H^4.(C^2H^3O^2)^2 \\ (C^2H^5)^3P\end{matrix}\right\} = \left.\begin{matrix}C^2H^3.C^2H^3O^2 \\ (C^2H^5)^3P\end{matrix}\right\} + C^2H^4O^2$$

If this be so, the second stage of the reaction is precisely similar to the decomposition already mentioned of the bromine-compound by heat.

d. By nascent hydrogen it is converted into bromide of tetrethylphosphonium:—

$$\left.\begin{matrix}C^2H^4Br^2 \\ (C^2H^5)^3P\end{matrix}\right\} + H^2 = \left.\begin{matrix}C^2H^5Br \\ (C^2H^5)^3P\end{matrix}\right\} + HBr$$

e. With derivatives of ammonia, it gives bodies of the type of the second compound. The following bodies have been so obtained.

$$\left.\begin{matrix}C^2H^4Br^2 \\ (C^2H^5)^3P \\ H^3N\end{matrix}\right\}, \left.\begin{matrix}C^2H^4Br^2 \\ (C^2H^5)^3P \\ CH^3.H^2N\end{matrix}\right\}, \left.\begin{matrix}C^2H^4Br^2 \\ (C^2H^5)^3P \\ C^2H^5.H^2N\end{matrix}\right\}, \left.\begin{matrix}C^2H^4Br^2 \\ (C^2H^5)^3P \\ (CH^3)^3N\end{matrix}\right\}, \left.\begin{matrix}C^2H^4Br^2 \\ (C^2H^5)^3P \\ (CH^3)^3P\end{matrix}\right\}, \left.\begin{matrix}C^2H^4Br^2 \\ (C^2H^5)^3P \\ (C^2H^5)^3P\end{matrix}\right\}, \left.\begin{matrix}C^2H^4Br^2 \\ (C^2H^5)^3P \\ (C^2H^5)^3As\end{matrix}\right\}$$

It has already been stated that bodies of this class part with all their bromine to salts of silver. Hydrate of silver gives $\left.\begin{matrix}C^2H^4.H^2.O^2 \\ 2[(C^2H^5)^3P]\end{matrix}\right\}$ and similar bodies. These are strong bases and give the corresponding salts by the action of acids. $\left.\begin{matrix}C^2H^4.H^2.O^2 \\ 2[(C^2H^5)^3P]\end{matrix}\right\}$ is decomposed by heat into $\left.\begin{matrix}C^2H^4O \\ (C^2H^5)^3P\end{matrix}\right\}$, a compound already mentioned, and oxide of

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* As rational names for bodies deriving from the mixed type $\left.\begin{matrix}\text{[illegible]}O \\ mH^3N\end{matrix}\right\}$, namely *amic bases* and *amic acids*, the terms *hydoramines* and *hydoramides* (not to be confounded with hydramides) may be used (see further, art. NOMENCLATURE).

triethylphosphine, $P(C^2H^5)^3O$.—$\left.\begin{matrix}C^2H^4Br^2\\(C^2H^5)^3P\\(C^2H^5)^3As\end{matrix}\right\}$ is decomposed by heat into $\left.\begin{matrix}C^2H^4Br^2\\(C^2H^5)^3P\end{matrix}\right\}$ and triethylarsine, $(C^2H^5)^3As$.

B. Action of Triatomic Chlorides, Bromides, or Iodides: —

1. *On Ammonia.*

Tribromide of glyceryl, $(\overset{\prime\prime\prime}{C^3}H^5)Br^3$, gives with ammonia a base containing $NC^6H^9Br^2$, and bromide of ammonium. The reaction probably takes place according to the following stages: —

$$1^\circ \qquad C^3H^5Br^3 = C^3H^4Br^2 + HBr.$$
$$2^\circ \quad 2(C^3H^4Br^2) + NH^3 = NC^6H^9Br^2 + 2HBr,$$

the hydrobromic acid which is formed of course combining with ammonia. The first stage of the reaction is analogous to the conversion of bromide of ethylene into bromethylene by the action of alcoholic potash: the compound, $C^3H^4Br^2$ may be regarded as dibrom-propylene, or as bromide of brom-allyl, $(C^3H^4Br)'Br$. In the latter case, the product of its action on ammonia becomes $N\left\{\begin{matrix}(C^3H^4Br)'\\(C^3H^4Br)'\\H\end{matrix}\right.$ *dibrom-diallylamine.* (Maxwell Simpson).

2. *On Primary derivatives of ammonia.*

Chloroform, $(\overset{\prime\prime\prime}{C}H)Cl^3$, reacts on phenylamine, forming the hydrochlorate of a monoacid base, containing, $C^{13}H^{12}N^2$, and which may be considered as representing two molecules of phenylamine in which the radicle $(\overset{\prime\prime\prime}{C}H)$ replaces H^3; thus $\left.\begin{matrix}(\overset{\prime\prime\prime}{C}H)\\(C^6H^5)^2H\end{matrix}\right\}N^2$.

3. *On Tertiary derivatives of ammonia.*

Iodoform, $(\overset{\prime\prime\prime}{C}H)I^3$, combines with three molecules of triethylphosphine, giving $\left.\begin{matrix}CH.I^3\\3[(C^2H^5)^3P]\end{matrix}\right\}$. This compound parts with all its iodine to silver-salts, which accords with what is said above respecting the compounds of bromide of ethylene with triethylphosphine. Its solution treated with hydrate of silver does not give a corresponding hydrate, but hydrate of methyl-triethylphosphonium and oxide of triethylphosphine.

$$\begin{matrix}(\overset{\prime\prime\prime}{C}H)I^3\\3[(C^2H^5)^3P]\end{matrix} + 3AgHO = \left.\begin{matrix}CH^3.HO\\(C^2H^5)^3P\end{matrix}\right\} + 2[(C^2H^5)^3P.O] + 3AgI.$$

C. Action of Tetratomic Chlorides, Bromides, or Iodides on Derivatives of Ammonia.

Bichloride of carbon, $(\overset{iv}{C})Cl^4$, reacts on phenylamine thus: —

$$\underset{\text{3 mol. phenylamine.}}{3(C^6H^7N)} + CCl^4 = 3HCl + C^{19}H^{17}N^3.HCl.$$

The product of this reaction may be regarded as the hydrochlorate of a base deriving from three molecules of phenylamine by the substitution of $(\overset{iv}{C})$ for H^4: viz.

$$\left.\begin{matrix}(\overset{iv}{C})\\(C^6H^5)^3\\H^3\end{matrix}\right\}N^3.$$

(For details, see various papers by Hofmann, Proc. Roy. Soc. vols. ix. and x., also the Articles Phosphorus, Arsenic, Antimony.)

Ammonium-bases containing Metals.—A very large number of compounds have been obtained by treating different metallic salts with ammonia. Some of these compounds are apparently of similar constitution to the salts of the organic ammonium-bases, or to easily conceivable derivatives of them. But it is impossible to reduce the greater number of them to any consistent system, before they have themselves been more thoroughly examined, and we have more definite notions as to the atomicity of the metals contained in them. The following are examples of some of these compounds which can be written as analogous to known or conceivable organic compounds.

Metallic Compounds.	*Organic Analogues.*
$N.H^3CuCl$	$N.H^3.C^6H^5.Cl$
$NH^2(\overset{''}{Hg})Cl$	$N.H^2(C^2H^5)^2Cl.$
(or $N^2H^4(\overset{''}{Hg})^2Cl^2$(?)	$N^2H^4(C^2\overset{''}{H}{}^4)^2.Cl^2.$
$N(\overset{''}{Hg})^2Cl$	$N(C^2H^5)^4Cl.$
(or $N^2(\overset{''}{Hg})^4Cl^2$ (?)	$N^2(C^2\overset{''}{H}{}^4)^4Cl^2.$
$NH^3\overset{''}{Hg}Cl^2$	$N(CH^3)^3(C^2\overset{''}{H}{}^4)Br^2.$
$\left.\begin{array}{l}N\\O\\I\end{array}\right\{\begin{array}{l}H^3\\(\overset{''}{Hg})\\(\overset{''}{Hg})\end{array}$	$\left.\begin{array}{l}N\\O\\I\end{array}\right\{\begin{array}{l}H^3\\(C^2\overset{''}{H}{}^4)\\(C^2\overset{''}{H}{}^4).\end{array}$ (unknown.)
$NH^3(\overset{''}{Pt})Cl^2.$	$P(C^2H^5)^3(C^2\overset{''}{H}{}^4)Br^2.$
$N^2H^6(\overset{''}{Pt})Cl^2$	$P^2(C^2H^5)^6(C^2\overset{''}{H}{}^4)Br^2.$

*** $Hg = 200$

The attempts which have been made by some chemists to make formulæ for many other metallic derivatives of the ammonium-salts, by supposing ammonium capable of replacing hydrogen in ammonium, or by assuming the existence of such radicles as PtCl or Pt*O*, may be described in words used with reference to another subject, by the author of one such attempt, as "unwissenschaftliche Spielereien, die hier keine Berücksichtigung verdienen." — G. C. F.

AMNIOTIC LIQUID. (See ALLANTOIC and AMNIOTIC LIQUIDS.)

AMOIBITE. A mineral allied to nickel-glance, and probably identical with it.

AMORPHISM. (Gm. i. 102.)—Solid bodies which do not exhibit any crystalline or regular structure, even in their minutest particles, are said to be *amorphous* (α, privative, and μορφη form). Such are opal and other forms of silica, also glass, obsidian, pumice stone, bitumen, resins, coal, albuminous substances, and numerous precipitates. Such bodies have a smooth conchoidal fracture, never exhibiting a granulated appearance on the broken surface; they have no particular planes of cleavage, such as are found in crystals, but require the same amount of force to separate them in all directions: they also conduct heat equally in all directions, and never exhibit double refraction, excepting when pressed or otherwise brought into a forced state. In short, the essential character of an amorphous body is perfect uniformity of structure in every direction, each particle being similarly related to all those which surround it, the character of a fluid without its mobility, whereas in crystallised or organised* bodies, the molecular forces act with greatest energy in certain lines or axes, thereby determining an arrangement of the particles according to fixed laws, and causing the body to exhibit different degrees of tenacity, elasticity, permeability, refracting power, and conducting power for heat and electricity in different directions. It must not be assumed that a body is amorphous because it does not exhibit a regular shape in the mass: marble and loaf-sugar have no definite external form; but they consist of aggregates of minute crystals, and when broken, exhibit, not a conchoidal, but a granular fracture.

The amorphous state is by no means peculiar to certain substances, a great number of bodies being capable of existing both in the amorphous and in the crystalline state. Sulphur, when it solidifies slowly from fusion or solution, forms regular crystals, but when poured in the melted state into cold water, it solidifies in a soft, plastic, viscid mass, capable of being drawn out into threads, and exhibiting no trace whatever of crystalline structure. Phosphorus also assumes a regular crystalline form when slowly cooled from solution in bisulphide of carbon or from fusion, but when cast into moulds and quickly cooled, it forms a waxy solid, having a conchoidal fracture; and by other modes of treatment to be described hereafter, it may be reduced to a perfectly amorphous red powder. Carbon is crystalline in the diamond and in graphite; amorphous in charcoal, lamp-black, and the various other forms which it assumes when

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* The term *amorphous* is generally used in contradistinction to *crystalline* alone; but its proper use is in opposition to *regular*, whether crystalline or organised: for organic structures exhibit many properties of which amorphous bodies, properly so called, are destitute; thus wood, according to the researches of Dr. Tyndall, exhibits three distinct axes of cleavage, permeability, elasticity, and conducting power for heat.

separated from organic bodies by imperfect combustion. Boron and silicon exhibit similar varieties. Arsenious acid, as it collects in the chimneys of furnaces in which arsenical ores are roasted, is a glassy amorphous mass; but by dissolving it in hot water or hydrochloric acid, and leaving the solution to cool, it is obtained in the crystalline form (see ARSENIC). Native sulphide of antimony, which is crystalline, may be rendered amorphous by melting it in a glass tube and plunging the tube into ice-cold water: and by melting it again and cooling slowly, the crystalline structure may be restored. Similar transformations may be effected with native sulphide of mercury, also with the minerals Vesuvian and Axinite, and certain varieties of garnet. Glass, which is perhaps the most characteristic of amorphous bodies, may be devitrified by keeping it for some time in the soft state at a high temperature: it then acquires a crystalline structure and becomes nearly opaque, forming the substance called Reaumur's porcelain. Generally speaking, rapid cooling from fusion is favourable to the assumption of the amorphous structure, while crystallisation is promoted by slow cooling, the particles then having time to arrange themselves in a definite manner. It is also true to a great extent that bodies which pass at once from the perfectly fluid to the solid state, — water, for instance, — crystallise on solidifying, whereas those which pass through the viscous form, like glass, solidify in the amorphous state; to this, however there are some striking exceptions: thus sugar, the solution of which is extremely viscid when concentrated, solidifies by slow evaporation in crystals of great size and regularity.

The passage from the amorphous to the crystalline state sometimes takes place spontaneously, the body all the while remaining solid. Vitreous arsenious acid, which, when recently prepared, is perfectly transparent, becomes turbid when left to itself for a few months, and subsequently white and opaque. Sugar which has been melted in the form of barley-sugar is in the vitreous state, but after a while acquires a crystalline structure and becomes opaque. These phenomena show that the molecules of bodies, even in the solid state, possess a certain freedom of motion.

The change from the amorphous to the crystalline condition, or the contrary, is generally accompanied by an alteration of other physical properties. Bodies are for the most part denser and less soluble in the crystalline than in the amorphous state, and have less specific heat. Vesuvian, which crystallises in square prisms of specific gravity about 3·4, and garnet, which occurs in rhombic dodecahedrons of specific gravity 3·63, both form by fusion and subsequent cooling, transparent glasses whose specific gravity is about 2·95, so that, in passing from the crystalline to the amorphous state, garnet suffers an expansion of about $\frac{1}{5}$ and vesuvian of $\frac{1}{8}$. The glass also dissolves readily in hydrochloric acid, whereas the crystallised minerals are quite insoluble. Many other crystalline siliceous minerals not soluble in acids become so by fusion, probably from the same causes. Quartz, which is crystallised silica, is much harder and denser than opal, which is the same chemical compound in the amorphous state. Quartz-powder dissolves but very slowly in boiling potash-ley and is quite insoluble in that liquid when cold, whereas pulverised opal is gradually dissolved at ordinary temperatures and in a few minutes at the boiling heat. A remarkable exception to the general rule is, however, presented by arsenious acid, which is both less dense and more soluble in the crystalline than in the vitreous state.

Another difference first observed by Graham is, that bodies have greater specific heat in the amorphous than in the crystalline state. Ordinary phosphate of sodium (PO^4Na^2H) solidifies from fusion in the vitreous state; the corresponding arsenate in the crystalline form: now the former in solidifying gives out perceptibly less heat in a given time than the latter, a greater portion of the latent heat of fusion appearing to be retained by it. Connected with this law is the remarkable phenomenon of incandescence which many bodies exhibit when their temperature is gradually raised. Hydrated oxide of chromium if heated merely to the point at which it parts with its water, remains nearly as soluble in acids as before, but if the heat be raised nearly to redness, the oxide suddenly becomes incandescent, and is afterwards found to be much denser and nearly insoluble in acids. Similar phenomena are exhibited by alumina and zirconia. Gadolinite (silicate of yttrium) which in its natural state exhibits a conchoidal fracture and obsidian-like appearance, becomes vividly incandescent when moderately heated, and is afterwards found to dissolve but very imperfectly in hydrochloric acid, although before ignition it is very easily soluble; its density increases at the same time, though its absolute weight remains unaltered. Vitreous arsenious acid also sometimes exhibits incandescence in passing from the amorphous to the crystalline state. When a solution of the vitreous acid in hot hydrochloric acid is left to cool in the dark, the formation of every crystal is accompanied by a flash of light; but a solution of the crystalline acid, under the same circumstances, exhibits no light whatever.

AMPELIC ACID. An acid isomeric with salicylic acid, $C^7H^6O^3$, obtained in small quantity by the action of strong nitric acid upon those schist-oils which boil between 80° and 150° C. Picric acid and a flocculent matter are formed at the same time. Ampelic acid is a white substance, without odour, nearly insoluble in cold water, but little soluble in boiling water. Its solution reddens litmus. Boiling alcohol and ether dissolve it readily, and on cooling deposit it in the form of a powder, having a scarcely perceptible crystalline character. Saturated with ammonia, it exhibits the following reactions. With chloride of calcium, a white precipitate, which does not form when hot; the mixture deposits crystals on cooling. No precipitate with the chlorides of barium, strontium, manganese, or mercury. A green precipitate with acetate of nickel; blue with acetate of copper; and white with acetate and nitrate of lead. (Laurent, Ann. Ch. Phys. [2] lxiv. 325.)

AMPELIN. A substance resembling creosote, obtained from that portion of schist-oil which boils between 200° and 280° C. The oil is shaken up several times with strong sulphuric acid, then mixed with $\frac{1}{15}$ or $\frac{1}{20}$ of its bulk of aqueous potash, and the liquid is left at rest for a day. The lower watery layer of liquid is then separated from the upper oily layer, and shaken up with dilute sulphuric acid, and the oil which rises to the surface is removed with a pipette, and gently heated with 10 or 20 times its bulk of water, which dissolves the ampelin, leaving a small quantity of oil. On separating this oil, and adding a few drops of sulphuric acid to the aqueous solution, the ampelin rises to the surface in the form of an oil, having a slight brownish tint.

Ampelin dissolves in 40 or 50 times its volume of water, and is separated from the solution by a few drops of sulphuric or nitric acid, even when very dilute. Potash, soda, and their carbonates render the solution slightly turbid at the first instant, but it recovers its transparency when heated. Carbonate of ammonium renders it permanently turbid. Chloride of sodium or chloride of ammonium added to a solution of ampelin in caustic potash or carbonate of potassium separates the ampelin, which is then not redissolved on heating the liquid. Ampelin dissolves in alcohol, and in all proportions in ether. It does not solidify at —20° C. It is decomposed by distillation, yielding water, a light oil, and charcoal. Boiling nitric acid attacks it strongly, producing oxalic acid, and an insoluble viscous substance. (Laurent, Ann. Ch. Phys. [2] lxiv. 321.)

AMPHIBOLE and **AMPHIBOLITE.** (See HORNBLENDE.)

AMPHID SALTS. A name applied by Berzelius to salts which, according to his views, are compounds of two *oxides*, *sulphides*, *selenides*, or *tellurides*, *e. g.* sulphate of copper, $Cu^2O.SO^3$; sulpharsenate of potassium, $3K^2S.As^2S^5$; sulphantimonate of sodium, $3Na^2S.Sb^2S^5$, &c.,—such salts containing three ultimate elements—in contradistinction to the haloid-salts, namely, the chlorides, bromides, iodides, &c., which are binary compounds of the first order, containing only two elements, such as chloride of sodium, NaCl, iodide of silver, AgI, &c. It is evident that the so-called amphid salts are those which belong to the *water-type*, *e. g.* nitrate of copper, $Cu^2O.N^2O^5 = O\left\{\begin{matrix}NO^2\\Cu\end{matrix}\right.$ Sulpharsenate of potassium, $3K^2S.As^2S^5 = S^3\left\{\begin{matrix}(AsS)'''\\K^3\end{matrix}\right.$, whereas the haloid-compounds belong to the type HH or HCl.

AMPHIGENE. See LEUCITE.

AMPHILOGITE. See DIDRIMITE.— **AMPHODELITE.** See ANORTHITE.

AMYGDALIC ACID, $C^{20}H^{28}O^{13}$.—Produced by the metamorphosis of amygdalin under the influence of alkalis. Amygdalin dissolves in cold baryta-water without decomposition, but on boiling the mixture, ammonia is disengaged. The ebullition is continued until the liberation of ammonia ceases altogether; a current of carbonic acid is then passed through the liquid, to precipitate the excess of baryta; and the acid is finally liberated from the barium-salt by cautious precipitation with sulphuric acid. It is a slightly acid liquid, which dries up to a gummy mass,—insoluble in absolute alcohol, cold or boiling, and insoluble in ether. Boiled with a mixture of peroxide of manganese and sulphuric acid, it yields formic and carbonic acids and hydride of benzoyl. Its salts are not well defined; they are more or less soluble in water. (Liebig and Wöhler, Ann. Ch. Pharm., lxiv. 185.)

Amygdalate of ethyl is obtained, according to Wöhler, by dropping a mixture of alcohol and amygdalin into hydrochloric acid gas. (Wöhler, Ann. Ch. Pharm. lxvi. 240.)

AMYGDALIN, $C^{20}H^{27}NO^{11} + 3H^2O$.—A crystalline principle existing in bitter-almonds, the leaves of the *Cerasus lauro-cerasus*, and many other plants, which by distillation yield hydrocyanic acid. The bitter-almond oil and hydrocyanic acid do not exist ready formed in these plants, but are the result of the decomposition of amygdalin under the influence of emulsin, a nitrogenised fermentable principle existing with it in the plant.

To prepare amygdalin,—the oil is expressed from the paste of bitter-almonds, and the residual mass extracted with boiling alcohol. This alcoholic solution is rendered turbid by the presence of globules of oil, which are allowed to collect and separated by decantation; it is then evaporated to half its original volume, and the amygdalin separated by the addition of ether, in which it is insoluble. The precipitated amygdalin is pressed between folds of bibulous paper, washed with ether, and finally crystallised from concentrated boiling alcohol. (Liebig and Wöhler.)

Amygdalin crystallises in white scales having a pearly lustre, insoluble in ether, but very soluble in water, from which it crystallises in thin transparent prisms containing 3 atoms of water of crystallisation. Its aqueous solution has a slightly bitter taste. It deflects the plane of polarisation of a ray of light to the left: $[a] = 35{\cdot}51$. The change which amygdalin undergoes by the action of emulsin (and other albuminous vegetable principles), is expressed by the following equation:

$$\underset{\text{Amygdalin.}}{C^{20}H^{27}NO^{11}} + 2H^2O = \underset{\substack{\text{Hydride}\\\text{of benzoyl.}}}{C^7H^6O} + \underset{\substack{\text{Hydro-}\\\text{cyanic}\\\text{acid.}}}{CNH} + \underset{\text{Glucose.}}{2C^6H^{12}O^6}$$

By distillation with nitric acid, or other oxidising agents, it is resolved into ammonia, hydride of benzoyl, benzoic, formic, and carbonic acids. Caustic alkalis convert it into amygdalic acid.

It is a neutral body, forming compounds neither with acids nor with alkalis.

AMYL, C^5H^{11}, or $C^{10}H^{22}$. (Gm. xi. pp. 1—83; Gerh. ii. pp. 675—708).—The fifth term of the series of alcohol-radicles, C^nH^{2n+1}. The alcohol in an impure state (potato-fusel oil), appears to have been first noticed by Scheele; and has been investigated, together with its derivatives, by Pelletan (J. Chim. med. i. 76, also Ann. Ch. Phys. [2] xxx. 200), Dumas (Ann. Ch. Phys. [2] lvi. 314; Dumas and Stas, Ann. Ch. Phys. [2] lxxiii. 128); Cahours (Ann. Ch. Phys. [2] lxx. 81, lxv. 193); and Balard, Ann. Ch. Phys. [3] xii. 294). The radicle itself was isolated by Frankland in 1849. (Chem. Soc. Qu. J. iii. 307; Ann. Ch. Pharm. lxxiv. 41.)

Amyl in the free state, $C^{10}H^{22} = C^5H^{11}.C^5H^{11}$, is prepared by the action of zinc-amalgam upon iodide of amyl, the reaction being completed by the addition of potassium (Frankland).—2. By the action of sodium upon iodide of amyl (Wurtz).—3. By the electrolysis of caproate of potassium (Brazier and Gossleth).—4. By the destructive distillation of certain kinds of coal (Greville Williams).

(1.) Pasty zinc-amalgam is brought into the copper cylinder used in the preparation of zinc-ethyl (see ETHYL): the cylinder is then half filled with granulated zinc and iodide of amyl is added. After gently warming to expel the air, the cylinder is closed and heated for several hours at about 170° C. After cooling, it is opened and potassium is added (about $\frac{1}{20}$th by weight of the iodide of amyl employed). The cylinder is again closed and heated for an hour at the same temperature. To obtain the amyl, the cylinder is heated in a water-bath at 80° C., whereupon amylene and hydride of amyl pass over. On applying the heat of a naked flame, amyl distils over, and may be purified by one rectification. (Frankland.)

(2.) Iodide of amyl is warmed with sodium, and distilled; the product again distilled from sodium and rectified, the portion which passes over at 158° C. being collected apart. (Wurtz, Ann. Ch. Phys. [3] xliv, 275.)

(3.) A concentrated solution of caproate of potassium is submitted to the electrolytic action of six zinc-carbon elements, the platinum poles being separated by a porous diaphragm. Amyl collects upon the surface of the liquid surrounding the negative pole: it is distilled from alcoholic caustic potash and washed with water. (Brazier and Gossleth, Chem. Soc. Qu. J. iii. 221.)

(4.) Bog-head naphtha is submitted to fractional rectification, the portion boiling between 154°—169° C. being collected apart, and the product thus obtained is submitted to the action of fuming nitric acid, the action of the acid being checked by cold. The mixture on standing separates into two layers, the upper of which is again shaken with nitric acid. The product which has remained unacted upon is washed with caustic soda and water successively, dried with solid caustic potash, and distilled over sodium. The resulting liquid is again rectified at 157°—160° C. (C. Greville Williams, Phil. Trans. 1857, 447.)

Amyl is a transparent colourless liquid, of agreeable smell and burning taste. Specific gravity, 0·77 at 11° C.—Boiling-point 155°—159° C. Vapour-density 4·90. It is miscible with alcohol, immiscible with water. Amyl is not acted upon by fuming sulphuric acid; it is slowly attacked by nitric and nitro-sulphuric acids, and decomposed after long digestion with pentachloride of phosphorus.

BROMIDE OF AMYL.—Prepared by the action of bromine and phosphorus upon amylic alcohol (Cahours, Ann. Ch. Phys. [2] lxx. 98). In three flasks are placed respectively 15 pts. of amylic alcohol, $2\frac{1}{2}$ pts. of bromine, and 1 pt. of phosphorus. A little of the bromine is added to the amylic alcohol, and the latter is poured upon and digested with the phosphorus to decoloration. It is then poured into its own flask, and a little more bromine is added. The process is repeated, and the final product is washed with water, dried, and rectified.

Bromide of amyl is a transparent colourless liquid, heavier than water. It has an alliaceous odour and sharp taste. It is soluble in alcohol, insoluble in water. Decomposes by boiling with alcoholic caustic potash.

CHLORIDE OF AMYL, $C^5H^{11}Cl$.—Obtained by the action of strong hydrochloric acid upon amylic alcohol (Balard, Ann. Ch. Phys. [3] xii. 294); also by the action of pentachloride of phosphorus upon amylic alcohol. (Cahours.)

Preparation.—1. Amylic alcohol is heated in a retort to 110° C., a rapid current of hydrochloric acid being passed through the tubulus into the amylic alcohol; the chloride of amyl as it is formed distils over. When the retort is nearly empty the distillate is poured back, and the same process repeated (Guthrie). The product is then shaken with strong hydrochloric acid, in which amylic alcohol is soluble, chloride of amyl insoluble,—then with water.

2. Amylic alcohol is distilled with its own weight of pentachloride of phosphorus, washed, dried, and rectified.

Chloride of amyl is a colourless, transparent, neutral liquid, of agreeable odour. It boils at 101° C. Vapour-density, 3·8. Burns with a luminous flame bordered with green.

Chlorine acts upon chloride of amyl, giving rise to substitution-products, which go as far as $C^5H^3Cl^8Cl$.

CYANIDE OF AMYL. See CYANIDES.

HYDRATE OF AMYL, or AMYL-ALCOHOL, $C^5H^{12}O = \left.\begin{matrix}C^5H^{11}\\ H\end{matrix}\right\}O$ [or $C^{10}H^{11}O^2 = C^{10}H^{11}O.HO$].—*Amylate of Hydrogen. Hydrate of Amyl. Hydrate of Pentyl. Hydrated Oxide of Amyl. Fusel-oil.*—This alcohol seems invariably to accompany ethylic alcohol (see ALCOHOLS, p. 97) when the latter is formed by fermentation. The conditions of its formation are unknown; it seems, however, to occur in largest quantity in those liquids which remain most alkaline during fermentation. In the distillation of vegetable juices which have been fermented, the latter portions of the distillate contain water, ethylic, propylic (?) butylic and amylic alcohols, besides the acids and aldehydes of these alcohols and probably higher fatty acids and aldehydes. To obtain the pure amylic alcohol from the crude product, it is shaken several times with hot milk of lime, decanted, dried over chloride of calcium, and rectified at 132° C.

Amylic alcohol is a transparent colourless liquid having a peculiar odour (the peaty smell of whisky is due to its presence in small quantities), which causes coughing, and burning taste. It burns with a white smoky flame. Solidifies at about − 22° C. Specific gravity 0·811 at 19° C. Boiling-point 132° C. Vapour-density 3·147. Soluble in common alcohol and ether, nearly insoluble in water. It dissolves small quantities of sulphur and phosphorus.

According to Pasteur (Compt. rend. xli. 296), ordinary amylic alcohol is a mixture of two amylic alcohols identical in chemical composition and vapour-density, but differing in their optical properties, one of them turning the plane of polarisation of a ray of light to the left, while the other is opticially inactive. A difference of solubility in some of the salts obtained from the mixed alcohols, furnishes the means of their separation; the active amyl-sulphate of barium is $2\frac{1}{2}$ times more soluble in water than the corresponding inactive salt. The optical rotatory power of amylic alcohol varies, on account of its being a variable mixture of these two modifications. This difference in the two amylic alcohols is said to be traceable in some other of their derivatives, *e. g.* caproic acid prepared from active cyanide of amyl, rotates the plane of polarisation. (Wurtz.)

Decompositions of Amyl-alcohol.—1. By *heat.* The vapour of amyl-alcohol passed through a glass tube heated to dull redness, is resolved into tritylene (propylene) marsh-gas and other hydrocarbons. (Reynolds.)

2. By *oxidation.*—Amyl-alcohol is difficult to set on fire, and burns with a white smoky flame. In contact with the air at ordinary temperatures, it is very slowly oxidised and acquires a slight acid reaction. The oxidation is greatly accelerated by the presence of platinum-black, the amyl-alcohol being then converted into valeric acid:

$$C^5H^{12}O + O^2 = C^5H^{10}O^2 + H^2O.$$

Amyl-alcohol distilled with a mixture of sulphuric acid and peroxide of manganese or bichromate of potassium, yields valeric aldehyde, valeric acid, and valerate of amyl. The same products, together with nitrite of amyl and hydrocyanic acid, are formed by the action of nitric acid. Amyl-alcohol is also converted into valeric acid by heating it to 220° C. with a mixture of lime and hydrate of potassium, hydrogen gas being evolved:

$$\underset{\text{Amyl-alcohol.}}{C^5H^{12}O} + KHO = \underset{\text{Valerate of potassium.}}{C^5H^9KO^2} + 4H.$$

3. By *sulphuric acid.*—Amyl-alcohol mixes readily with strong sulphuric acid, forming a red liquid, which contains amylsulphuric acid, $SO^4.C^5H^{11}.H$, as well as free sulphuric acid. On distilling the mixture, the amyl-alcohol is dehydrated, and amylene, C^5H^{10} passes over, together with the polymeric compounds, $C^{10}H^{20}$ and $C^{20}H^{40}$, and perhaps also amylic ether, $(C^5H^{11})^2O$; at the same time, however, a portion of the alcohol is oxidised and converted into valeric aldehyde and valeric acid, sulphurous acid being evolved and a black pitchy mass remaining in the retort.

4. With *phosphoric acid*, amyl-alcohol yields amyl-phosphoric acid, $PO^4.C^5H^{11}.H^2$.—Distilled with phosphoric anhydride, it is converted into amylene and its multiples.

5. *Trichloride of phosphorus* converts amyl-alcohol into phosphite of amyl, amylphosphorous acid, chloride of amyl, and hydrochloric acid:

$$3(C^5H^{11}.H.O) + PCl^3 = \underset{\text{Phosphite of amyl.}}{PO^3.(C^5H^{11})^2.H} + C^5H^{11}Cl + 2HCl.$$

$$\text{and} \quad 3(C^5H^{11}.H.O) + PCl^3 = \underset{\text{Amylphosphorous acid.}}{PO^3.C^5H^{11}.H^2} + 2C^5H^{11}Cl + HCl.$$

6. With *pentachloride of phosphorus*, amyl-alcohol forms chloride of amyl, hydrochloric acid, and chlorophosphoric acid, or, when the amyl-alcohol is in excess, diamylphosphoric acid:

$$C^5H^{11}.H.O + PCl^5 = C^5H^{11}Cl + HCl + \underset{\text{Chlorophosphoric acid.}}{POCl^3}$$

$$\text{and } 9(C^5H^{11}.H.O) + 2PCl^5 = 5C^5H^{11}Cl + 5HCl + 2\underset{\text{Diamylphosphoric acid.}}{[PO^4.(C^5H^{11})^2.H]} + H^2O.$$

7. *Chlorine-gas* is absorbed in large quantity by amyl-alcohol and forms chloramylal, a compound homologous with chloral.—8. Amyl-alcohol absorbs *hydrochloric acid gas* and mixes with the concentrated aqueous acid; on heating the mixture chloride of amyl is formed.—9. It dissolves, with the aid of heat, in a concentrated aqueous solution of *chloride of zinc*, forming a liquid which boils at 130°C., and yields a distillate of amylene and its multiples.—10. Distilled with *phosphorus* and *bromine* or *iodine*, it yields bromide or iodide of amyl.—11. Distilled with *fluoride of boron*, or *fluoride of silicon*. it yields amylene and its multiples, but little or no oxide of amyl.—11. *Phosgene gas* is abundantly absorbed by amyl-alcohol, forming chloroformate of amyl, and the liquid when distilled yields carbonate of amyl (**Medlock**) [*with evolution of phosgene* (?)]

$$C^5H^{11}.H.O + \underset{\text{Phosgene.}}{COCl^2} = \underset{\text{Chloroformate of amyl.}}{CClO^2.C^5H^{11}} + HCl.$$

$$\text{and} \quad 2(CClO^2.C^5H^{11}) = \underset{\text{Carbonate of amyl.}}{CO^3.(C^5H^{11})^2} + COCl^2 \quad [?]$$

Carbonate of amyl is also obtained by adding water to the solution of phosgene in amyl-alcohol (**Medlock**):

$$2(CClO^2.C^5H^{11}) + H^2O = CO^3.(C^5H^{11})^2 + 2HCl + CO^2.$$

21. *Disulphide of carbon*, in presence of *potash*, converts amyl-alcohol into amylsulphocarbonic or amylxanthic acid (p. 206).—13. *Chloride of cyanogen* is rapidly absorbed by amyl-alcohol, and forms products similar to those which it yields with ethyl-alcohol.

$$\underset{\text{Amyl-alcohol.}}{C^5H^{12}O} + CNCl + H^2O = \underset{\text{Amyl-urethane.}}{C^6H^{13}NO^2} + HCl.$$

14. Potassium (and sodium) decomposes amyl-alcohol in the same manner as ethyl alcohol, forming amylate of potassium, $C^5H^{11}KO$ with evolution of hydrogen.

Amyl-alcohol combines with a few metallic chlorides in the same manner as ethyl-alcohol. With *chloride of calcium* and *dichloride of tin*, it forms crystalline compounds which are decomposed by water. It dissolves in caustic potash and soda.

HYDRIDE OF AMYL, $C^5H^{11}.H$.—Iodide of amyl is heated with zinc and its own volume of water for a few hours to 142° C. in a copper cylinder (see zinc-ethyl), and the contents are distilled from a water bath at 60°. The distillate consists principally of amylene and hydride of amyl. The mixture is left for 24 hours in contact with caustic potash, and again rectified from a water-bath at 35°. The distillate is immersed in a freezing mixture and treated with a mixture of anhydrous and fuming sulphuric acid, which retains the amylene. Lastly, the hydride of amyl is distilled from a water-bath (Frankland, Ann. Ch. Pharm. lxxiv. 41). Colourless transparent liquid, having a pleasant odour. Specific gravity 0·638, at 14° C. Boiling-point 30° C. Vapour-density 2·382.

Iodide of Amyl, $C^5H^{11}I$.—Prepared by the action of iodine and phosphorus upon amylic alcohol (Cahours, Ann. Ch. Phys. [2] lxx. 81). Four parts of iodine are placed in one flask, and excess of phosphorus in another. Seven parts of moist amylic alcohol are poured upon the iodine, the liquid shaken till opacity is produced, then poured upon the phosphorus and digested till the colour is removed—again poured upon the iodine, and so on, till all the iodine is exhausted. The nearly colourless product so obtained, is washed with slightly alkaline water, dried over chloride of calcium and rectified. The latter portions are the purest.

Iodide of amyl is a colourless transparent liquid of faint odour and pungent taste. Specific gravity 1·511 at 11° C. Boiling-point 146°. Vapour-density 6·675. It turns brown on exposure to light.

Oxide of Amyl, $C^{10}H^{22}O = (C^5H^{11})^2O$ [or *$C^{10}H^{11}O$*]. — *Amylic ether. Amylate of Amyl.* — Prepared by the action of sulphuric acid on amyl-alcohol. Strong sulphuric acid is heated to 150° C. in a retort. and amyl-alcohol allowed to enter slowly through the tubulus; the distillate is then shaken with carbonate of sodium, washed and rectified.—2. By the action of amylate of potassium on iodide of amyl. Amylate of potassium is digested in a retort connected with an inverted condenser, with an equivalent quantity of iodide of amyl, and the product is distilled and rectified.—3. By the dry distillation of amylsulphate of calcium (Kekulé). Oxide of amyl boils at about 180° C. It is colourless and of agreeable odour.

Oxide of Amyl and Ethyl, $C^7H^{16}O = C^2H^5.C^5H^{11}.O$. *Amylate of Ethyl, Ethylate of Amyl, Ethylamylic Ether.* Prepared by the action of amylate of potassium upon iodide of ethyl, or of iodide of amyl upon ethylate of potassium. (Williamson, Chem. Soc. Qu. J. iv. 103, 234.)—(1.) A known weight of potassium is dissolved in absolute alcohol in a tubulated retort; iodide of amyl is added in sufficient quantity for there to be rather less than 1 at. of iodine for every at. of potassium in the ethylate of potassium; the retort is connected with an inverted condenser; and the contents are digested for some time. After distillation, water is added, and the liquid which separates out is dried and rectified.—(2.) Iodide of ethyl is added to a hot solution of potash in amylic alcohol, digested &c., as in 1 (Guthrie). Amylate of ethyl is a colourless transparent liquid of agreeable odour, similar to that of sage. It is lighter than water. Boiling-point 112° C. Vapour-density 4·04.

Amylate of Methyl, or *Methylate of Amyl*, $C^6H^{14}O = CH^3.C^5H^{11}.O$, is prepared in the same manner as (1) amylate of ethyl (Williamson). Boils at 92° C. Vapour-density 3·74.

Amylate of Potassium, $C^5H^{11}KO$. — On bringing freshly cut potassium into dry amylic alcohol, the potassium is dissolved and hydrogen is evolved. To obtain this body in a state of purity, the action is aided by heat until the mass becomes viscid. Any globules of metal which have remained unacted upon are removed, and the product is poured upon a cold slab, and allowed to solidify. It is then strongly pressed between many folds of bibulous paper to remove the unaltered amylic alcohol.

Amylate of potassium is a crystalline white body, soapy to the touch, and alkaline to the taste. It is soluble in the alcohols. By water it is instantly converted into amylic alcohol and hydrate of potassium.

Amylate of sodium, $C^5H^{11}NaO$. Closely resembles amylate of potassium.

Sulphides of Amyl. *Protosulphide of Amyl.* $(C^5H^{11})^2S$ or $C^{10}H^{22}S$.—Equivalent quantities of amylsulphate and monosulphide of potassium are intimately mixed in a retort (by solution and evaporation) and distilled (Balard, Ann. Ch. Phys. [3] xii. 248). Colourless liquid of offensive odour. Boiling-point 216° C. Vapour-density 6·3.

Disulphide of Amyl, $C^5H^{11}S$.—Obtained by distilling together amylsulphate and disulphide of potassium (O. Henry, Ann. Ch. Phys. [3] xxv. 246). Amber-coloured liquid. Boiling at about 250°. Specific gravity ·918 at 18° C.

Sulphide of Amyl and Hydrogen: Amyl-mercaptan, $C^5H^{11}.H.S$ [or *$C^{10}H^{11}S.HS.$*] Prepared by saturating caustic potash with sulphuretted hydrogen, adding the product to crude amylsulphate of potassium (prepared by mixing equal weights of amylic alcohol and sulphuric acid, neutralising with carbonate of potassium and filtering) and distilling from a capacious retort in a chloride of calcium bath. The oily drops in the distillate are washed, dried, and rectified (Kreutzsch, J. pr. Chem. xxxi. 1). Colourless liquid of intolerable odour. It is soluble in alcohol and ether, but insoluble in water. Specific gravity 0·845 at 0° C. Boiling-point about 120° C. Vapour-density 3·631. It combines with metallic oxides.

Amylmercaptide of mercury is obtained as a colourless liquid on bringing amylmercaptan in contact with mercuric oxide. The mixture solidifies to a solid mass on cooling. The compound is insoluble in water, but soluble in boiling alcohol. The other amylmercaptides are not distinctly known.

Sulphide of Carbonyl, Amyl, and Hydrogen. Amylsulphocarbonic acid. Amylxanthic acid. $C^6H^{12}S^2O = \left.\begin{array}{c}(CO)''\\ C^5H^{11}.H\end{array}\right\} S$.—The free acid is prepared from the potassium-salt by treating the aqueous solution of the latter with dilute hydrochloric acid (Balard, Ann. Ch. Phys. [3] xii. 307). Light yellow oily liquid, of penetrating odour, heavier than water, acid to test paper. It is quickly decomposed by water.

Amylxanthate of potassium, $C^6H^{11}.K.S^2O$.—A cold saturated solution of hydrate of potassium in amylic alcohol, is treated with bisulphide of carbon until the alkaline reaction has disappeared, and the yellow crystals of the potassium-salt which separate out on cooling, are washed with ether, and dried between blotting paper.

The ethyl and methyl salts of amylxanthic acid, are formed by digesting equivalent quantities of ethylsulphate or methylsulphate of potassium, with amylsulphocarbonate of potassium. They are oily liquids lighter than water. (Johnson, Chem. Soc. Qu. J. v. 142.)

Dioxysulphocarbonate of Amyl, $C^6H^{11}S^2O$.—The compound so-called, which contains 1 at. hydrogen less than amylxanthic acid, is produced by the action of iodine on amylxanthate of potassium. It is an oily liquid which boils at 187° C, undergoing decomposition at the same time, and yielding among other products amylxanthate of amyl, $CS^2O.(C^5H^{11})^2$. Digested with aqueous ammonia, it yields *amylxanthate of ammonium*, and *xanthamylamide* or *sulphocarbamate of amyl*, $\left.\begin{array}{r}(CS)''H^2\\ C^5H^{11}\end{array}\right\}\begin{array}{l}N\\ O\end{array}$

$$\underbrace{2C^6H^{11}S^2O}_{\text{Dioxysulpho-carbonate of amyl.}} + 2NH^3 = \underbrace{CS^2O.C^5H^{11}.NH^4}_{\text{Amylxanthate of ammonium.}} + \underbrace{C^6H^{13}NSO}_{\text{Xanthamylamide.}} + S.$$

The last mentioned compound, *xanthamylamide*, is a yellow neutral oil, which boils at 184° C. but not without decomposition, being resolved by distillation into amylmercaptan and cyanuric acid:

$$3C^6H^{13}NSO = 3C^5H^{12}S + C^3N^3H^3O^3.$$

Heated on platinum foil, it burns with a yellow luminous flame, giving off white vapours. Boiled with hydrate of barium, it is resolved into amyl-alcohol and sulphocyanide of barium:

$$C^6H^{13}NSO + BaHO = C^5H^{12}O + CNSBa + H^2O;$$

similarly with potash. It is decomposed by chlorine and by nitric acid.

Xanthamylamide is insoluble in water, but dissolves readily in alcohol and ether. It unites with chloride of mercury, forming the compound $C^6H^{13}NSO.4HgCl$, which crystallises in white feathery crystals. With dichloride of platinum dissolved in water, it forms a yellow precipitate. (M. W. Johnson, Chem Soc. Qu. J. v. 142.)

Amysulphocarbamic acid, $C^6H^{13}NS^2$ (see next page).

TELLURIDE OF AMYL, or TELLURAMYL, $(C^5H^{11})^2.Te$. has been obtained in an impure state by distilling telluride of potassium with amylsulphate of calcium. It is a liquid having a strong disagreeable odour, and boiling at about 198° C. but decomposing at the same time, and depositing tellurium in small shining prisms. By exposure to the air it is converted into a white mass. The nitrate of telluramyl is a colourless heavy oil, obtained by heating telluramyl with moderately strong nitric acid. Treated with the bromide, chloride, or iodide of hydrogen or sodium, it yields the corresponding compounds of telluramyl in the form of viscid heavy oils. The chloride treated with oxide of silver, yields *oxide of telluramyl* in the form of an oily liquid soluble in water, and so strongly alkaline that it separates ammonia from salammoniac. It forms a crystalline salt with sulphuric acid. (Wöhler and Dean, Ann. Ch. Pharm. xcvii. 1.)—F. G.

AMYLAMINES:

AMYLAMINE, $C^5H^{13}N = C^5H^{11}.H^2.N$. *Amylammonia, Amylia.*—This organic base is formed: (1.) By heating cyanate or cyanurate of amyl with caustic potash (Wurtz, Ann. Ch. Phys. [3] xxx. 447):

$$\underbrace{CNO.C^5H^{11}}_{\text{Cyanate of amyl.}} + \underbrace{2KHO}_{\text{Hydrate of potassium.}} = \underbrace{C^5H^{13}N}_{\text{Amylamine.}} + \underbrace{CO^3K^2}_{\text{Carbonate of potassium.}}.$$

(2.) In the destructive distillation of animal substances (Anderson).—(3.) By heating amylsulphate of potassium with alcoholic ammonia to 250° C. (Berthelot).—(4.) By the dry distillation of leucine, carbonic anhydride being at the same time evolved (Schwanert, Ann. Ch. Pharm. cii. 221):

$$\underbrace{C^6H^{13}NO^2}_{\text{Leucine.}} = \underbrace{C^5H^{13}N}_{\text{Amylamine.}} + CO^2$$

Also by carefully distilling a solution of horn in strong caustic potash, leucine being then formed and afterwards decomposed as above (Schwanert).—(5.) By the action of caustic potash on flannel, tetrylamine being also found among the products. (Gr. Williams, Chem. Gaz. 1858, 310.)

Preparation.—Cyanate or cyanurate of amyl (obtained by distilling cyanate of potassium with amylsulphate of potassium) is distilled with strong caustic potash; the distillate is neutralised with hydrochloric acid, evaporated and recrystallised; and the hydrochlorate of amylamine decomposed by distillation from lime and rectified over hydrate of barium. Colourless liquid. Specific gravity 0·75 at 18° C. Boiling-point 94° C. Amylamine precipitates most metallic oxides which are precipitable by ammonia; it redissolves alumina.

Carbonate of amylamine is formed as a crystalline solid, when its base is exposed to the carbonic acid of the air.—*Hydrobromate of amylamine*, $C^5H^{13}N.HBr$, or *bromide of amylium*, $C^5H^{14}NBr$, is formed by adding hydrobromic acid to the base.—*Hydrochlorate of amylamine*, $C^5H^{13}N.HCl$ or *chloride of amylium*, $C^5H^{14}NCl$, forms with dichloride of platinum a double salt, $C^5H^{14}NCl.PtCl^2$, which is soluble in boiling water.

Amylsulphocarbamate of Amylium, $C^{11}H^{26}N^2S^2 = \left.\begin{matrix}(CS)''.H.C^5H^{11}\\ N(H^3.C^5H^{11})\end{matrix}\right\}\begin{matrix}N\\ S\end{matrix}$, is produced by the union of 2 molecules of amylamine with 1 molecule of bisulphide of carbon: ($C^{11}H^{26}N^2S^2 = 2C^5H^{13}N + CS^2$). The mixture of the two substances becomes warm, and on cooling deposits the compound in white shining scales, insoluble in water and in ether, but easily soluble in alcohol. At 100° C. it decomposes after a while, giving off sulphuretted hydrogen. Treated with hydrochloric acid, it yields chloride of amylium, and *amylsulphocarbamic acid* $\left.\begin{matrix}(CS)''.H.C^5H^{11}\\ H\end{matrix}\right\}\begin{matrix}N\\ S\end{matrix}$, which is an oily body, soluble in ether, ammonia and potash; mixed with amylamine, it reproduces the original salt. (A. W. Hofmann, Chem. Soc. Qu. J. xiii. 60.)

DIAMYLAMINE, $(C^5H^{11})^2HN$.—When amylamine is heated to 100° C. with bromide of amyl, direct combination occurs, and the solid hydrobromate of diamylamine is formed. The base is obtained by distillation of the bromide with caustic potash (Hofmann, Phil. Trans. 1851, p. 357). Slightly soluble in water. Boiling-point about 170°. The salts of diamylamine are difficultly soluble in cold water, more readily in hot water.

TRIAMYLAMINE, $(C^5H^{11})^3N$, is obtained by heating diamylamine with bromide of amyl, and distilling the so-formed bromide of triamylium with caustic potash (Hofmann). Its properties and those of its salts are similar to those of diamylamine. It boils at about 257° C.

TETRAMYLIUM, $N(C^5H^{11})^4$. *Tetramylammonium.*—Ammonium in which the whole of the hydrogen is replaced by amyl. Not known in the separate state, but obtained as an iodide by the action of iodide of amyl on triamylamine, the mixture solidifying, after three or four days' boiling, into an unctuous crystalline mass. The iodide of tetramylium is also produced, but very slowly, by heating iodide of amyl in a sealed tube with strong aqueous ammonia. This salt, $N(C^5H^{11})^4I$, dissolves sparingly in water, forming an extremely bitter liquid, from which it is precipitated in the crystalline form by alkalis. Boiled with oxide of silver, it yields a very bitter alkaline solution of the *hydrate of tetramylium*:

$$N(C^5H^{11})^4.I + AgHO = AgI + \left.\begin{matrix}N(C^5H^{11})^4\\ H\end{matrix}\right\}O.$$

On mixing the liquid with potash, or concentrating it strongly by evaporation, the hydrate of tetramylium rises to the surface in the form of an oily layer, which gradually solidifies. A moderately concentrated solution of the base left to evaporate in an atmosphere free from carbonic acid, deposits the hydrate in definite crystals sometimes an inch long, and containing several atoms of water of crystallisation. These crystals when heated, melt in their water of crystallisation, and ultimately leave the pure hydrate in the form of a semi-solid transparent mass. At higher temperatures, the hydrate is completely decomposed, giving off water, triamylamine, and a hydrocarbon, which is probably amylene:

$$\underbrace{N(C^5H^{11})^4H.O}_{\text{Hydrate of tetramylium.}} = H^2O + \underbrace{N(C^5H^{11})^3}_{\text{Triamylamine.}} + \underbrace{C^5H^{10}}_{\text{Amylene.}}$$

Hydrate of tetramylium dissolves readily in acids, forming solutions which yield crystalline salts by evaporation. The sulphate crystallises in long, capillary threads: the nitrate in needles, the oxalate in large deliquescent plates, the chloride in laminæ with palm-like ramifications; the chloroplatinate, $(C^5H^{11})^4NCl.PtCl^2$, in beautiful orange-yellow needles. (Hofmann, Chem. Soc. Qu. J. iv. 316.)—F. G.

(For the *Amyl-phosphines*, *Arsines*, and *Stibines*, see PHOSPHORUS, ARSENIC, and ANTIMONY.)

AMYLENE. C^5H^{10}, or $C^{10}H^{10}$.—This hydrocarbon, a homologue of ethylene or olefiant gas, and the fifth term of the series, C^nH^{2n}, is produced by the dehydration of amylic alcohol by sulphuric acid, phosphoric anhydride, or chloride of zinc, also by the dry distillation of amyl-sulphate of calcium (Kekulé). To prepare it, a concentrated aqueous solution of chloride of zinc is heated to 130° C., with an equal volume of amylic alcohol: and the product is distilled from a water-bath over caustic potash, and repeatedly rectified (Balard, Ann. Ch. Phys. [3] xii. 320). It is a transparent colourless, very thin liquid, having a faint but offensive odour. Boils at 39° C. (Balard); at 35° (Frankland); at 42° (Kékulé). Vapour-density, 2·68 (Balard), 2·386 (Frankland), 2·43 (Kékulé); (by calculation, for 2 vol. = 2·4265). The vapour is rapidly and completely absorbed by sulphuric anhydride and pentachloride of antimony (Frankland). It possesses anæsthetic properties, and has been tried as a substitute for chloroform, but has been found to be very dangerous, having in more than one instance led to fatal results.

Amylene is diatomic, like ethylene, uniting with 2 at. Br, NO^2, HO, &c., and with 1 at. O, S, &c.

ACETATE OF AMYLENE, $C^9H^{16}O^4 = \left.\begin{matrix}(C^5H^{10})''\\(C^2H^3O)^2\end{matrix}\right\}O^2$, is produced by heating the bromide $C^5H^{10}Br^2$, with a mixture of acetate of silver mixed with glacial acetic acid:

$$C^5H^{10}Br^2 + 2(C^2H^3O.Ag.O) = 2AgBr + \left.\begin{matrix}C^5H^{10}\\(C^2H^3O)^2\end{matrix}\right\}O^2.$$

It is a colourless neutral liquid, insoluble in water, boiling above 200° C. and easily decomposed by alkalis into acetic acid and amylene-glycol. (Wurtz, Ann. Ch. Phys. [3] lv. 458.)

BROMIDE OF AMYLENE, $C^5H^{10}Br^2$, is produced by passing bromine-vapour into amylene. Heated in a sealed tube with alcoholic ammonia, it forms bromide of ammonium, and *bromamylene*, C^5H^9Br. — By treating amylene with a larger quantity of bromine, another compound is formed, containing $C^5H^9Br^3$, probably *dibromide of bromamylene*, $C^5H^9Br.Br^2$. This compound, treated with alcoholic potash, yields *dibromamylene*, $C^5H^8Br^2$. (Cahours, Ann. Ch. Phys. [3] xxxviii. 90.)

HYDRATE OF AMYLENE, OR AMYLENE-GLYCOL, $C^5H^{12}O^2 = \left.\begin{matrix}(C^5H^{10})''\\H^2\end{matrix}\right\}O^2$.—Prepared by distilling acetate of amylene with dry pulverised hydrate of potassium, and purified by a second distillation in the same manner, and subsequent rectification *per se*:

$$\left.\begin{matrix}C^5H^{10}\\(C^2H^3O)^2\end{matrix}\right\}O^2 + 2KHO = 2(C^2H^3KO^2) + \left.\begin{matrix}C^5H^{10}\\H^2\end{matrix}\right\}O^2.$$

It is a colourless, very syrupy liquid, having a bitter taste with aromatic after-taste. When cooled with a mixture of solid carbonic acid and ether, it solidifies into a hard transparent mass. It does not affect polarised light. Its specific gravity is 0·987 at 0° C. It boils at 177°, and distils without alteration. When pure it dissolves in water in all proportions. The aqueous solution turns acid when exposed to the air in contact with platinum-black, yielding chiefly carbonic acid, with only a small quantity of a fixed acid, apparently butylactic acid. When gently heated with nitric acid, it is rapidly oxidised, the chief product of the action being butylactic acid, $C^4H^8O^3$. (Wurtz, *loc. cit.*)

Amylene-glycol, treated with hydrochloric acid, either gaseous or aqueous, is converted, slowly at ordinary, more quickly at higher temperatures, into the *chlorhydrin of amylene-glycol*, $C^5H^{10}.HO.Cl$. This compound cannot be isolated, but remains dissolved in the excess of acid and is decomposed by distillation. The acid solution treated with potash yields oxide of amylene.

NITRYLIDE OF AMYLENE, $C^5H^{10}(NO^2)^2$. *Nitroxide of Amylene.*—Obtained by passing peroxide of nitrogen (nitryl, NO^2, prepared by heating anhydrous nitrate of lead) into a flask containing amylene, and surrounded by a freezing mixture. The gas is instantly absorbed, and the amylene is gradually converted into a pasty mass of minute crystals, which may be purified by washing with cold alcohol, recrystallisation from boiling ether and drying in vacuo over sulphuric acid. It gave by analysis, 37·26 per cent. C, 6·51 H, and 17·66 N; the formula requiring 37·09 C, 6·18 H, and 17·28 N.

The compound may also be obtained, though less advantageously, by passing vapour of amylene mixed with air into fuming nitric acid. It is remarkable as affording the first example of the direct combination of nitryl, (NO^2), with an organic radicle.

Heated by itself in a dry tube, it decomposes at about 95° C., giving off nitrous anhydride, N^2O^3, and nitrous acid, HNO^2, and leaving a heavy liquid apparently containing nitrate of amyl. Heated with quick lime, it gives off an aromatic body, probably consisting of oxide of amylene. (Guthrie, Chem. Soc. Qu. J. xiii. 45, 129.)

OXIDE OF AMYLENE, $(C^5H^{10})''.O$, a volatile liqnid, isomeric with valeric aldehyde, It boils at 95° C. Has a pleasant ethereal odour, and a rough taste. Specific gravity in the liquid state, 0·8244 at 0° C. Vapour-density by experiment 2·982, by calculation (2 vol.) = 2·805. It burns easily, with a yellow flame. It is insoluble in *water*, and is not converted into amylene-glycol when heated with water in a sealed tube. It dissolves in *alcohol*, in *ether*, and in a mixture of the two. It mixes with *acids*. It unites with *anhydrous* or *crystallisable nitric acid* at a higher temperature, but the combination is attended with partial decomposition. (A. Bauer, Compt. rend. li. 500.)

AMYLENE WITH SULPHUR AND CHLORINE:

1. *Dichlorosulphide of Amylene*, $C^5H^{10}SCl^2$, or $C^{10}H^{10}S^2Cl^2$.—Protochloride of sulphur (SCl^2) is brought into a flask surrounded with ice and an excess of amylene added very gradually. The excess of amylene is evaporated off,—the residue digested and washed with water, dissolved in ether, filtered, and evaporated. It is a non-volatile liquid, having a pungent odour, insoluble in water, soluble in ether and alcohol. Specific gravity, 1·149 at 12° C. Distilled with excess of alcoholic caustic potash, it yields amylene, *disulphide of fusyl* (C^5H^9S), and other products.

2. *Disulphochloride of Amylene*, $C^5H^{10}SCl$, or $C^{10}H^{10}S^2Cl$.—On treating disulphide of chlorine (SCl), with excess of amylene, and evaporating the latter, a transparent yellow, non-volatile liquid, of faint and nauseous odour is obtained, having the above composition. It is obtained pure by digestion with water, solution in ether, filtration, and evaporation. Specific gravity, 1·149 at 12° C. Soluble in ether, absolute alcohol, and sulphide of carbon. (Guthrie, Chem. Soc. Qu. J. xii. 112.)

Disulphochloride of amylene treated with chlorine, gives off hydrochloric acid, and is converted into a non-volatile liquid, of specific gravity 1·406 at 16° C., miscible with ether, insoluble in water, but soluble in hot alcohol. This liquid gave by analysis numbers agreeing approximately with the formula, $C^{10}H^7Cl^4S$, which may be that of *chlorosulphide of trichloramylene*, $C^{10}(H^7Cl^3).SCl$, or that of *sulphide of tetrachloramyl*, $C^{10}(H^7Cl^4)S$. (Guthrie, Chem. Soc. Qu. J. xiii. 43.)

AMYLENE WITH SULPHUR AND OXYGEN:

Disulphoxide of Amylene, $C^{10}H^{10}S^2O$.—Prepared by digesting the disulphochloride in alcoholic solution with protoxide of lead, till all the chlorine is combined, dissolving in ether, filtering and evaporating. Specific gravity, 1·054 at 13° C. Non-volatile, yellow, or almost colourless. Soluble in ether and alcohol, insoluble in water.

Hydrate of Disulphoxide of Amylene, $C^{10}H^{10}S^2O.HO$.—Disulphochloride of amylene is heated in alcoholic solution for some hours, in a current of ammonia; the liquid is then poured off from the chloride of ammonium formed, and heated for some hours in a sealed tube to 100° C. with alcoholic ammonia; the excess of alcohol is driven off in a water-bath; the residue treated with water; and the oil which is thereby precipitated is washed with water. Yellow liquid of meaty odour. Somewhat soluble in hot water, soluble in alcohol and ether. Non-volatile. Specific gravity 1·049 at 8°. (Guthrie, Chem. Soc. Qu J. x. 120.)—F. G. and H. W.

ANACARDIC ACID, $C^{44}H^{64}O^7$. or $C^{44}H^{32}O^7$.—This acid is contained, together with cardol, in the pericarps of the cashew nut (*Anacardium occidentale*). The pericarps are extracted with ether, which dissolves out both the anacardic acid and the cardol; the ether is distilled off, and the residue, after being washed with water to free it from tannin, is dissolved in 15 or 20 times its weight of alcohol. This alcoholic solution is digested with recently precipitated oxide of lead, which removes the anacardic acid in the form of an insoluble lead-salt. The lead-salt is suspended in water, and decomposed by sulphide of ammonium, and from the solution of anacardate of ammonium, obtained after the removal of the sulphide of lead by filtration, the anacardic acid is liberated by the addition of sulphuric acid. After repeated purification by solution in alcohol, conversion into a lead-salt, and decomposition of this salt by hydrosulphuric acid, the acid is obtained as a white crystalline mass, which melts at 26° C. It has no smell, but its flavour is aromatic and burning. When heated to 200° C. it is decomposed, producing a colourless very fluid oil. It burns with a smoky flame, stains paper, and liquefies by prolonged contact with air, emitting an odour similar to that of rancid fat. Alcohol and ether dissolve it readily, and these solutions redden litmus.

Some of its salts are crystalline, others amorphous. The silver-salt is a pulverulent white precipitate, soluble in alcohol, in presence of a free acid. It contains two atoms of metal, $C^{44}H^{62}Ag^2O^7$. The lead-salt, obtained by mixing a boiling alcoholic solution of anacardic acid with an alcoholic solution of acetate of lead, is said to contain $C^{44}H^{60}Pb^4O^7$ or $\mathit{C^{44}H^{60}Pb^2O^7}$; if this formula be correct, the acid is tetrabasic [or dibasic, if the smaller atomic weights of carbon and oxygen are used]. The salts of ammonium, potassium, barium, calcium and iron, have been described, but they are not very definite, and their formulæ have not been fixed. (Städeler, Ann. Ch. Pharm. lxiii. 137.)

ANALCIME, $\left.\begin{matrix}Na^2\\Al^4\end{matrix}\right\}4SiO^3 + H^2O = Na^2O.SiO^2 + Al^4O^3.3SiO^2 + H^2O$ or $3\mathit{NaO.2SiO^3} + 3(\mathit{Al^2O^3.2SiO^3}) + 2\,\mathit{HO}$.—A mineral belonging to the zeolite family containing, according to H. Rose's analysis, 55·7 per cent. of silica, 13·5 soda, 23·0 alumina, and 8·3 water, which agrees very nearly with the preceding formula. It belongs to the regular system. Primary form a cube; it occurs also in leucite-octahedrons, and in cubes with the faces of the leucite-octahedron replacing the solid angles. Cleavage indistinct, parallel to the faces of the cube. Specific gravity from 2·1 to 2·2. Softer than felspar. In its purest form, it is colourless and transparent, but sometimes white inclining to grey or flesh-colour. According to Brewster, it polarises light in a peculiar manner, indicating a grouping of the molecules very different from that which is usually found in the regular system. Before the blowpipe, it loses water and becomes milk-white; but when the heat is increased, it becomes clear again, and then melts quickly to a transparent glass. It is readily decomposed by hydrochloric acid, with separation of viscid silica; after ignition, however, the decomposition is less easy. Analcime occurs frequently in clefts and geodes in granite, trap-rocks and lava. It is found on the Calton Hill, Edinburgh, at Talisker in the Isle of Sky, in Dumbartonshire, in the Ferroe Islands, in the Harz, and in Bohemia.

ANALYSIS—INORGANIC.

The object of chemical analysis is to ascertain the composition of any substance whatever. The distinction usually made between organic and inorganic compounds, has led to a corresponding division into organic and inorganic analysis: the latter being confined to the investigation of inorganic or mineral compounds. The methods employed in this branch of analysis, are far more numerous and varied than those hitherto devised for the analysis of organic compounds. Inorganic analysis is divided into qualitative and quantitative analysis. The former teaches us how to ascertain the elements of a substance with regard to their quality only, and how to separate them one from another: the latter establishes the methods of proceeding, by which we determine the relations of weight or volume, which these elements bear to one another. It is obvious that, before we can proceed to estimate the quantities of each element contained in a compound, we must know what are the elements that it contains: hence qualitative must always precede quantitative analysis.

Analysis is one of the most recent of the various branches of chemical science. Considerable progress had already been made in synthetical chemistry, in the preparation of chemical compounds, &c. at a time when the foundations of analytical chemistry (in the sense at present attached to the term) had not even been laid. Less than a century ago, when the properties and compounds of many elements were either entirely unknown or but imperfectly established, few problems were more difficult than that of inorganic analysis: the analyst had need of both penetration and caution in the highest degree, in order to discriminate between known and unknown substances. It is only within a comparatively recent period, that the discovery of many new elements, and the more complete investigation of the reactions of those already known, have enabled us to construct a systematic course of analysis, circumscribed within definite and well established rules.

Analytical chemistry, as we have already observed, aims at two objects, each closely connected with the other:—1. To ascertain what are the elements contained in substances whose composition is unknown:—2. To determine the relative proportions of those elements whose existence has previously been qualitatively ascertained. In the earliest analytical researches, both these objects were pursued simultaneously. Hence, in the very brief sketch of the history of analytical chemistry, which it is now our purpose to give, it is not possible to trace the progress of each of these branches of analysis independently of the other. For this purpose it is more convenient to adopt the distinction of analysis *in the wet* and *in the dry way* (*vide infra*): for these two branches of analysis aimed originally at different objects, and the progress of each was in great measure independent of that of the other.

The earliest analytical methods of which we have any information were in the dry way. They were directed exclusively to the separation of noble from ignoble metals; and they were generally conducted quantitatively, the object being to determine the commercial value of alloys, &c., by extracting the amount of the most precious metal contained in them. As early as the second century B.C., Agatharchides of Cnidos (quoted by Diodorus Siculus) gives an account of a method employed by the Egyptians for the extraction and purification of gold, which closely resembles the process of cupellation, at present so extensively employed for the separation of silver from lead. Strabo (about the Christian era) describes the extraction of silver from its ores by fusion with lead; and all the analytical methods which we meet with in the course of several successive centuries are but modifications of the same process. We find a description of the process given by Geber in the latter half of the eighth century, which corresponds very closely with that at present employed.

Strictly speaking, the employment of analysis in the dry way for qualitative purposes, is of much later date, commencing from the observation of the behaviour of different metallic compounds when exposed to a high temperature in contact with certain reagents, commonly called fluxes. It is to Pott, Professor of Chemistry at Berlin, circ. 1750, that we owe the first distinct record of these observations; he pointed out that it was possible, by the addition of certain fluxes, to fuse many substances which were infusible alone; and that the colour of the fused mass afforded information as to the nature of the original substance. This method of experimenting, which was conducted by him in crucibles and furnaces, on a comparatively large scale, received an immense extension by the introduction of the blowpipe, by means of which far more accurate indications were obtained with a much smaller quantity of the original substance. The first mention of this implement occurs about 1660, in the Memoirs of the Academia del Cimento, at Florence, when it is noticed as being employed by glass-blowers; and the first indication of its use for chemical purposes, is found in Kunkel's *Ars vitraria experimentalis*, 1679. Cramer, a German chemist, in his *Elementa Artis docimastica* (1739), gives the earliest instructions for its use as an implement of analysis. The further investigation of the results to be attained by means of this invaluable instrument, was effected mainly by a succession of Swedish chemists, of whom Cronstedt and Bergman were perhaps the most remarkable; and it is to Berzelius that the establishment of the existing system of blowpipe analysis was finally owing.

According to the present course of analysis, the method by the dry way is usually employed only in the preliminary examination: the cases are very rare in which its results can be relied upon for complete information as to all the constituents of a substance. For this purpose, recourse is now invariably had to analysis *in the wet way*. The early history of this method of analysis is very obscure, amounting in fact to nothing but the enumeration of a few random reactions, in the employment of which no system was observed. It was originally employed solely for the qualitative detection of adulterations in drugs, &c. It was next directed to the examination of mineral waters, to which purpose it was mainly confined until the latter half of the seventeenth century, at which period the first true perception of the problem involved in analytical chemistry was obtained by Boyle, who gave to this branch of the science the name by which it is at present designated. He was the first to establish clearly the idea of a chemical element, and to seek for methods of ascertaining what elements or known compounds are contained in any substance of unknown composition. Although these methods comprise many reactions which were known before his time, still he has the credit of being the first to generalise these scattered facts, and to collect them into a coherent system. Among the new reactions introduced in his time, we may mention the precipitation of calcium-salts by sulphuric acid, as serving for the detection of either calcium or sulphuric acid; of silver-salts by hydrochloric acid, as a test for both silver and chorine; that of iron with tincture of galls; the blue colour of copper-salts with excess of ammonia, &c. Since the time of Boyle, analytical chemistry, in the hands of Marggraf, Scheele, Bergman, Klaproth, H. Rose, &c. has made continual advances, the enumeration of which cannot be attempted in a brief historical summary like the present; until by degrees it has assumed the systematic form of which we shall presently proceed to give an outline.

The establishment of quantitative analysis, as a distinct branch of chemical science, is of comparatively recent date. For a long time it was almost entirely neglected, little if any importance being attached to the relative proportions in which elements exist in a compound. Until the latter half of the last century, it was confined to the purpose of assaying, or of determining approximately the value of ores; and it was not until Lavoisier, with such triumphant success, employed the balance as a means of refuting old errors and of establishing new truths, that inquiries into the quantitative composition of bodies came to be regarded as the only sure test and foundation for chemical theory. Almost all the quantitative analyses by which any reliable knowledge of the constitution of substances has been obtained, are included in this period, and date within the last 60 or 70 years. The empirical results thus obtained, have led to the discovery of the most important theoretical truths, *e.g.* the theory of atoms and equivalents, the law of multiple proportions, &c., which in turn have been of inestimable value in controlling the results of analysis, and ensuring to them a degree of accuracy which could never have been attained by merely empirical determinations.

Until a comparatively recent period, the only method of quantitative analysis was that *by weight*. By this method, the substance to be estimated is either weighed directly, or in the form of some compound of known composition, from whose weight that of the substance to be estimated is readily calculated, the reagent by which the substance is separated being always employed *in excess*. More recently, another method has been introduced, which depends upon the employment of only the exact quantity of the reagent which is necessary to produce the reaction desired; and upon the determination of this quantity, not by weight, but by measure. This method, known as the *Volumetric method of analysis* (see ANALYSIS VOLUMETRIC), is only applicable in cases where the point at which the reaction is complete can be determined accurately by means of some distinctly visible phenomenon occurring in the solution to be analysed. The first introduction of this method is due to Descroizilles, who, at the close of the last century, applied it to the valuation of bleaching powder by means of indigo-solution: since which time it has been gradually extended until it has grown into a distinct and most important branch of analysis, which, in most cases, is at least equal in accuracy to the method by weight, while it is greatly superior in speed and facility of execution.

The methods of qualitative analysis consist in bringing the substance under examination into contact with other bodies of known properties, and observing the phenomena which ensue. These phenomena consist in alterations, either in state of aggregation, form, or colour, depending upon some chemical change. All bodies which we employ for this purpose, we call by the general name of *reagents*, the ensuing phenomena are called *reactions*. Acids, bases, salts, and simple bodies (elements) are alike used as reagents.

By means of reagents, the chemist puts questions to the substance under examination, enquiring whether it contains this or that group of chemically similar elements, or only this or that member of such group. If the question be put correctly—*i.e.* if all the conditions under which the reaction expected can be produced by the reagent employed be carefully observed, the answer is decisive as to the presence or absence of the element, or group of elements, sought: if, on the other hand, these conditions—*i.e.* the properties and chemical relations of the bodies formed by the chemical changes which constitute the reaction, have been wholly or partially neglected, the answer, if not certainly erroneous, is at least of doubtful accuracy.

Reagents may be employed either in *the wet way* or in *the dry way*. In the wet way, the reagent in solution, *i.e.* in the liquid form, is brought into contact with the substance to be examined, which is also in the liquid form. In the dry way, the two bodies are brought together in the solid state, and subjected to a high temperature. Of the utmost importance in analysis by the latter method, is the knowledge of the use of the blowpipe, and of the behaviour of bodies in the different flames which can be produced by it. (See BLOWPIPE.)

Many reagents exhibit the same, or a similar behaviour, with a certain fixed number, *i.e.* with a *group*, of elements, and with most of the compounds of these elements; and can therefore, be employed for the division of the elements into groups. Such reagents are termed *general reagents*. Others serve for the further distinction of the several members of such groups: their selection depends upon the knowledge of the special characteristic behaviour to such reagents of each single element, or of each of its several compounds. Such reagents are called *special* or *characteristic reagents*. Their number is much greater than that of the general reagents, their nature being as various as that of the substances which can come under examination: their selection depends upon the solubility or insolubility, colour, or other physical or chemical properties of the new compounds to which they give rise. They may frequently be employed reciprocally: thus, starch is a characteristic test for iodine, and reciprocally, iodine is a characteristic test for starch.

The analyst has not only to establish that this or that body is present in a compound, but he has also to prove that no other body is present besides those which he has actually found. Hence it is evident that he must not treat the substance under examination with any reagent indiscriminately. He must follow a certain fixed order, a methodical system, in the application of reagents, which will be the same for all inorganic substances whatever, let their elements be what they may. This systematic method, which cannot be departed from or abbreviated without danger, except in certain cases by the experienced chemist, consists in the employment of general reagents for the successive elimination of groups of elements possessing certain common chemical properties; and finally, in the recognition of each member of such groups by the employment of characterisric reagents. If the object be not a complete and accurate analysis, but merely to establish the presence or absence of some particular body, the characteristic reagent may in many cases be employed at once, without previous recourse to general reagents.

The first thing to be done in the qualitative analysis of a solid body, is to subject it to a preliminary examination in the dry way, by which means important information as to its composition may frequently be obtained: after which it is dissolved, and its constituents ascertained by examination in the wet way. The course of qualitative analysis, therefore, consists of 3 parts:

I. Preliminary examination in the dry way.
II. Solution, or conversion into the liquid form.
III. Analysis of the solution in the wet way.

We shall now proceed to treat successively of each of these operations.

I. *Preliminary Examination.*

This consists partly in an accurate observation of the physical properties of the substance (its form, colour, hardness, specific gravity, &c.): but chiefly in observing its behaviour *at a high temperature*, either alone, in contact with air, or with some chemical compound which produces either decomposition or simple solution.

1. *The substance is heated alone in a dry test-tube, on charcoal, or on platinum-foil.* — Water, sulphur and its acids, ammonium-, arsenic-, and mercury-compounds are completely volatilised. Carbon burns when heated in the air. If water is evolved, observe whether it is acid or alkaline to litmus. If gases are evolved, observe whether they are combustible: and if so, whether their combustion is sustained or intermittent. Organic compounds are decomposed by heat, generally with evolution of inflammable gas and separation of carbon: when heated with strong sulphuric acid and bichromate of potassium, they evolve carbonic anhydride, which gives a white precipitate with lime- or baryta-water. Bodies which are very rich in oxygen, nitrates, chlorates, perchlorates, bromates, iodates, deflagrate when heated on charcoal. Most alkaline, and some alkaline-earthy salts, melt without volatilising or changing colour; after strong ignition, the residue is alkaline to test-paper. Many silicates (especially zeolites) melt when a thin fragment of them is exposed in platinum-tongs to the blowpipe flame. Borates and alum swell up: other salts, *e. g.* chloride of sodium, decrepitate. Of metals: antimony, lead, tin, bismuth, cadmium, zinc, tellurium, fuse readily before the blowpipe, giving an incrustation of oxide; gold, silver, and copper, fuse with difficulty, and give no incrustation; iron, nickel, cobalt, molybdenum, wolfram, and platinum metals are infusible. The oxides and salts of the earthy and alkaline-earthy metals are infusible, or difficultly fusible; they become vividly incandescent, with a white light, but do not change colour; the earths, after ignition, are not alkaline to test-paper. The oxides and salts of some metals assume a darker colour when heated: those of zinc, tin, titanium, columbium (niobium), and antimony, become yellow: those of lead, bismuth, mercury (and chromates), become dark-brown.

2. *The substance, after ignition on charcoal, is moistened with a drop of a solution of nitrate of cobalt, and again strongly heated before the blowpipe.*—Alkaline phosphates borates, and silicates, give a *blue glass:* the earths, earthy phosphates, silica and many silicates give a *blue infusible mass:* zinc-oxide and titanic anhydride become *yellowish-green:* binoxide of tin, *bluish-green:* antimonic and columbic anhydrides, *dirty-green:* magnesia and tantalic anhydrides, *flesh-red:* baryta, *brown* or *brick-red:* glucina, lime, and strontia, *grey.*

3. *The substance is heated on platinum-wire (if a metallic salt, on charcoal) in the inner blowpipe flame, and the colour of the outer flame observed.*—A *yellow* colour indicates sodium: a *violet*, potassium: a *carmine-red*, lithium or strontium. The yellow colour imparted by sodium, completely overpowers those of the other alkaline metals: but, if the flame be observed through dark blue glass, the yellow rays are cut off, and the colours of potassium and lithium are plainly visible, even in presence of a large excess of sodium. A *reddish-yellow* colour indicates *calcium;* a *yellow-green*, barium or molybdenum; a *green*, cupric oxide, phosphoric, boric, or tellurous acid; a *blue*, arsenic, antimony, lead, selenium, or cupric chloride. In many cases, the colour is rendered more apparent if the substance be previously moistened with hydrochloric acid, or a

little chloride of silver added: phosphates and borates should be moistened with sulphuric acid.

The delicacy and sharpness of these chromatic indications are greatly increased by a method of observation lately introduced by Bunsen and Kirchhoff. It consists mainly in igniting a metallic salt on platinum wire, in a feebly luminous and nearly monochromatic flame, such as that of a Bunsen's gas-burner, and observing the flame through a prism. Very characteristic spectra are then produced, containing luminous coloured bands coincident in position with certain of Fraunhofer's lines. *Sodium* gives a spectrum reduced to a single bright narrow band; *lithium*, a bright red and a fainter yellow band; *potassium*, a spectrum nearly resembling the ordinary solar spectrum in the middle, but characterised by a bright line near the red extremity, and a fainter line near the violet end of the spectrum. The *strontium* spectrum consists of a broad bright orange band, with some fainter red bands; the *calcium* spectrum, of a broad bright green band, a somewhat narrower bright orange band, and some fainter yellow bands; and that of *barium*, of several bright green, yellow and orange with two faint red bands. The sodium reaction is extremely delicate, sufficing for the detection of a quantity of sodium as small as $\frac{1}{3000000}$ of a milligramme; distinct indications are likewise obtained with $\frac{9}{100000000}$ of a milligramme of lithium, $\frac{1}{1000}$ milligramme of potassium and barium, $\frac{6}{100000}$ milligramme of strontium, $\frac{6}{100000000}$ milligramme of calcium. (For details see the article LIGHT; also Pogg. Ann. cx. 161; Chem. Soc. Qu. J. xiii. 270.)

4. *The substance is heated on charcoal in the reducing flame with carbonate of sodium, or with carbonate of sodium and cyanide of potassium.*—Most arsenic compounds give a smell of garlic. All sulphur-, selenium-, and tellurium-compounds, give an alkaline sulphide, selenide, or telluride, which, when moistened, leaves a black stain on a clean silver plate. Tin-, silver-, copper-, and gold-compounds give malleable shining scales: compounds of nickel, cobalt, iron, molybdenum, wolfram, and the platinum-metals are reduced to a grey infusible powder: no incrustation is formed in any of these cases. Antimony-compounds give a *brittle* metallic globule, and a white incrustation: bismuth, a *brittle* globule and a brown-yellow incrustation: lead, a *malleable* globule, and a yellow incrustation. Zinc and cadmium are not reduced to the metallic state, but give, the former a white incrustation, not volatile in the outer flame, the latter, a brown-red incrustation.

5. *The substance is heated in a glass tube, open at both ends, held obliquely.*—The following substances yield gases having a peculiar smell: sulphides, of burning sulphur; selenides, of horseradish; arsenides, of garlic; many ammonium-salts, of ammonia; fluorides (especially on addition of microcosmic salt), of hydrofluoric acid. A metallic sublimate indicates arsenic- or mercury-compounds: a white sublimate is given by arsenides (crystalline), by antimonides and tellurides, (fusible), and by many ammonium-salts. A fused sublimate is given by the higher sulphides (brown-yellow), by selenides and selenium (blackish-red), and by sulphide of arsenic (yellow). All hydrated salts or substances containing hygroscopic water yield drops of water, the acid or alkaline reaction of which should be ascertained.

6. *The substance is heated in contact with metallic zinc and dilute hydrochloric or sulphuric acid.*—Many metallic acids are reduced to lower oxides by this treatment, a change of colour being produced. Titanic acid gives a *violet* colour: tungstic acid, and the chlorides of tantalum and columbium, a *blue*: molybdic acid, *blue*, changing to *green* and dark-brown: columbous acid, *blue*, changing to *dark brown*: chromic acid, *green*, iodic acid, *brown*, or if starch be added, *blue*.

II. *Solution of Solid Bodies.*

After having ascertained by the preliminary examination in the dry way, to what class of bodies the substance under examination belongs, the next step is to bring it into the liquid form, in other words, to *dissolve* it. In order to effect this, it is generally necessary, when the nature of the substance allows it, to reduce it to a fine powder by pounding in a mortar, and, if necessary, by subsequent levigation with water. This is indispensable in the case of minerals, especially of silicates, and of all other difficultly soluble, insoluble, or difficultly decomposible compounds. If the substance contains organic matter, this should be removed before proceeding further, as its presence materially interferes with the reactions of many mineral compounds. This may generally be effected by heating the substance strongly for some time in contact with air (more speedily with oxygen), until the whole of the carbon is converted into carbonic anhydride. In many cases, the oxidation of the carbon is facilitated by dropping nitric acid on the heated substance.

The solvents which are usually employed in the analysis of inorganic bodies are water, hydrochloric and nitric acids, and aqua-regia. The finely-powdered substance is first boiled with from 12 to 20 times its weight of *distilled water*, in order to ascertain its complete or partial solubility or insolubility therein. If it be not completely dissolved, the solution is filtered off from the residue, and a drop or two of it evaporated to dryness on platinum-foil, when, if the substance is partially soluble in water, a distinct residue is left; if the substance is completely insoluble, there is no residue after evaporation. In the former case, the solution is tested with litmus paper to see whether it has a neutral, acid, or alkaline reaction, and set aside for further examination. The portion insoluble in water is then treated successively with *dilute* and *concentrated hydrochloric acid*, particular attention being paid to the nature of the gases, if any, thereby evolved, and to the separation of solid products of decomposition. Carbonates evolve carbonic anhydride, with effervescence; peroxides, chromates, and chlorates evolve chlorine; cyanides, hydrocyanic acid; many sulphides, hydrosulphuric acid; sulphites and hyposulphites, sulphurous anhydride, with separation of sulphur in the latter case. Most metals (iron, zinc, tin, &c.) evolve hydrogen; or, if arsenic or antimony be present, arsenide or antimonide of hydrogen. If hydrochloric acid does not completely dissolve the substance, it generally effects the complete separation of one or more elements; for which reason the solution should be separated from the residue, and examined apart. The residue may consist of compounds undecomposible by hydrochloric acid, which existed in the original substance; or of insoluble compounds formed by the decomposition of the original substance by hydrochloric acid. Thus sulphur is separated from polysulphides, pulverulent or gelatinous silica from many silicates, tungstic acid from tungstates, &c.; or if lead, silver, or subsalts of mercury be present, insoluble chlorides of these metals will be formed.

If the substance is not completely soluble in hydrochloric acid, the insoluble residue is treated successively with *nitric acid* and *aqua regia*. In many cases (*e. g.* with phosphates, arsenates, silicates, tungstates, &c.), these compounds act merely as solvents; on many other bodies they exert an oxidising action. Thus, most sulphides, when treated with nitric acid, separate sulphur, which, by prolonged digestion with the acid, collects into yellow globules which swim on the surface of the liquid, or disappears altogether, being oxidised into sulphuric acid, which may be detected in the solution, unless it forms an insoluble salt with the dissolved metal. Sulphide of lead is converted by nitric acid into sulphate of lead: sulphides of antimony and tin into white oxides: protosulphide of mercury is insoluble in nitric acid, readily soluble in aqua regia. Most metals are completely soluble in nitric acid: the only metals not attacked by it are gold, platinum, and the rarer metals found in platinum-ores (with the exception of palladium, which is slowly soluble in nitric acid). Gold and platinum are soluble in aqua regia. Tin and antimony are not dissolved by nitric acid, but are converted into white oxides, insoluble in the acid; they are readily soluble in aqua regia (or hydrochloric acid and chlorate of potassium), if excess of nitric acid be avoided.

When a finely powdered substance is neither dissolved by successive treatment with the above solvents, nor so decomposed or attacked by them as to give an idea of its nature, it must be *rendered soluble*, in order that its constituents may be determined in the wet way. The method of doing this frequently depends upon the results of the preliminary examination. The following are the principal insoluble (or difficultly soluble) substances.

1. *Sulphates* (of barium, strontium, calcium, and lead). When heated on charcoal with carbonate of sodium, they give an alkaline sulphide: sulphate of lead gives also a malleable metallic globule; it is blackened by sulphide of ammonium, and soluble in basic tartrate of ammonium. They are rendered soluble by fusion with 3—4 pts. alkaline carbonate: after treating the fused mass with water, the solution contains the acid as alkaline sulphate, and the residue the base, as carbonate, which is now soluble in hydrochloric acid. In this and in all the following cases, the substance must be powdered as finely as possible before fusion. The sulphates of strontium, calcium, and lead are decomposed (the first not completely), by digestion with a solution of sodic carbonate: sulphate of calcium is somewhat soluble in water.

2. *Silica and silicates.*—When heated before the blowpipe with microcosmic salt, they swim undissolved in the fused bead. They are rendered soluble by fusion with 3—4 pts. alkaline carbonate (or hydrate of barium), treatment with hydrochloric acid, and evaporation with free acid, when the silica remains insoluble; or by treatment with hydrofluoric and sulphuric acids.

3. *Fluorides* (fluorspar, &c.)—When gently heated with concentrated sulphuric acid, they evolve hydrofluoric acid, which corrodes glass: if silica be present, fluoride of silicium is evolved, which gives a precipitate on contact with water. They are decomposed by fusion with 4 pts. alkaline carbonate, with addition of silica if necessary.

4. *Alumina* or *Aluminates.*—They give a blue infusible mass when heated with cobalt-solution. They are rendered soluble by fusion with 3—4 pts. acid sulphate of potassium.

5. *Chromic oxide* (chrome-iron-ore).—It gives a green bead in both flames with borax or microcosmic salt. Chrome-iron-ore is decomposed by successive fusion with acid sulphate of potassium, and with alkaline carbonate and nitre.

6. *Binoxide of tin*, and *Antimonic anhydride*.—They are coloured yellow by sulphide of ammonium, and dissolved by digestion in excess of the reagent: when heated on charcoal with sodic carbonate, they yield, the first a malleable, the second a brittle, metallic globule. They are rendered soluble in acids by fusion with 3—4 pts. alkaline carbonate.

7. *Tantalic*, *tungstic*, *titanic*, and *columbous anhydrides*.—They give with microcosmic salt a blue, violet, or (in presence of iron) a blood-red, bead: with zinc and hydrochloric acid, a coloured solution. They are rendered soluble by fusion with 6 pts. acid sulphate of potassium.

8. *Chloride, bromide, iodide, of silver; Sulphides of molybdenum, lead, &c.*—Chloride, bromide, and iodide of silver, are soluble in cyanide of potassium: when heated on charcoal with sodic carbonate, they yield metallic silver. Insoluble sulphides give off sulphurous anhydride when heated: sulphide of molybdenum gives a yellowish-green bead with microsmic salt, and is converted by roasting into molybdic anhydride, which gives a blue colour with zinc and hydrochloric acid.

9. *Metals* (osmide of iridium, or residues of platinum-ores).—The insoluble substance has metallic lustre, or is a black powder, not affected by ignition. It is rendered soluble by mixture with chloride of calcium and ignition in a stream of chlorine; or by fusion with potash and chlorate of potassium.

10. *Carbon*.—The insoluble substance is black (as diamond, colourless): it disappears when strongly ignited in an open platinum crucible, or before the blowpipe. It detonates when fused with nitre, forming carbonate of potassium; and yields carbonic anhydride when ignited with oxide of copper.

If the preliminary examination furnishes no distinct idea as to the nature of the insoluble substance, it must be fused with four times its weight of carbonates of potassium and sodium, the fused mass exhausted with water, and the residue treated with hydrochloric acid. If the substance contains any easily reducible metal (arsenic, antimony, tin, lead, bismuth, &c.) it must not be fused in a platinum crucible.

III. *Qualitative Analysis of Solutions.*

The first steps to be taken in the qualitative analysis of solutions are to ascertain whether the solution is neutral, acid, or alkaline to test paper; and whether it contains any non-volatile constituents. For the latter purpose, a small portion of it is carefully evaporated on platinum-foil: when, if non-volatile compounds are present, a residue is left which does not disappear when strongly heated, and should be submitted to the preliminary examination above described.

These precautions are of course unnecessary when the solution has been made by the analyst himself, as described in Section II.: but they should never be neglected when the substance to be examined is already in the liquid form, since, if carefully performed, they may enable him to conclude at once as to the presence or absence of whole groups of bodies. Thus it is evident that a solution which, after *careful* evaporation, leaves no fixed residue, cannot contain any non-volatile metallic salts. A solution *neutral* to test-paper can generally contain only salts of the alkaline or alkaline-earthy metals, since the salts of most other metals have an acid reaction. An *alkaline* solution (in which no non-volatile organic compounds are present), cannot contain any metals whose salts are insoluble in alkaline liquids: if the alkaline reaction be caused by the presence of an alkaline carbonate, the presence of the alkaline-earthy metals is impossible. If, however, non-volatile organic compounds are present, an alkaline solution may contain salts of copper or sesquisalts of iron, as well as such oxides, cyanides, sulphides, &c., as are soluble in cyanide of potassium or alkaline sulphides. The presence of certain acids implies the absence of certain metals, and *vice versâ*: thus the same acid solution cannot contain sulphuric acid and barium, hydrochloric acid and silver, &c. Silver need not be looked for in an alloy soluble in hydrochloric acid, nor gold, antimony, tin, &c. in one soluble in nitric acid.

It is advisable, when possible, to examine for acids and metals in separate portions of the solution.

a. Examination for Metals.

The systematic course of examination for metals which is now almost exclusively employed, depends upon the behaviour of metallic salts in solution towards the following general reagents: *hydrochloric acid*, *hydrosulphuric acid*, *sulphide of ammonium*, and *carbonate of ammonium*. It will be observed that all these reagents are volatile; so that in their application no substance is introduced into a solution which cannot be removed by simple elevation of temperature. Their application depends upon the different solubility of metallic chlorides and sulphides, and of the carbonates of the alkaline-earthy and alkaline metals. By means of these general reagents, as we have already observed, the metals are divided into certain groups, which are successively eliminated from the solution under examination; by which proceeding the detection of each individual member of each group is considerably facilitated. The following are the groups into which the metallic elements are thus divided:

α. Metals whose *chlorides* are insoluble, or difficultly soluble in water or dilute acids. These are lead, silver, and mercury (the last as sub-salts). These metals are not generally classed in a group by themselves, but are included in the group next following, to which they also belong.

β. Group 1.—Metals whose *sulphides* are insoluble in water or in dilute acids. They are all precipitated from their slightly acid solution by hydrosulphuric acid. They are further divided into two subdivisions according to the behaviour of their sulphides to sulphide of ammonium.

Subdivision A.—Metals whose sulphides possess acid properties. Their sulphides are soluble in alkaline sulphides (sulphides of ammonium, potassium, or sodium), forming therewith soluble sulpho-salts, which are generally analogous to the oxygen salts of the same metals, oxygen being replaced by sulphur. They are arsenic, antimony, tin, gold, platinum, iridium, selenium, tellurium, molybdenum, wolfram, vanadium.

Subdivision B.—Metals whose sulphides do *not* possess acid properties, not combining with alkaline sulphides, and so being insoluble therein. They are lead, silver, mercury, bismuth, copper, cadmium, palladium, rhodium, osmium, ruthenium. (Sulphide of mercury is soluble in sulphide of potassium or sodium: sulphide of copper is somewhat soluble in sulphide of ammonium.)

γ. Group 2.—Metals which are not precipitated by hydrosulphuric acid, but which are precipitated by sulphide of ammonium, from acid solutions. This group also is further subdivided.

Subdivision A.—Metals which are precipitated as *sulphides*. They are nickel, cobalt, manganese, iron, uranium, zinc. Their sulphides are insoluble in water, but soluble in dilute acids, with evolution of hydrosulphuric acid: hence they are not precipitated *at all* by hydrosulphuric acid from acid solutions, and not completely from neutral solutions. They are however completely precipitated from an acid solution by sulphide of ammonium, the acid being neutralised by the ammonia contained in it.

Subdivision B.—Metals which are precipitated as *hydrates*. They are aluminium, glucinum or beryllium, zirconium, thorium, yttrium, erbium, terbium, cerium, lanthanum, didymium: titanium, tantalum, columbium, chromium. (The first ten metals in this subdivision are known as *metals of the earths*, or *earthy metals*). They do not combine with sulphur in the wet way, and so are not precipitated by hydrosulphuric acid under any circumstances. Their hydrates, however, being insoluble in water, are precipitated from their neutral or acid solutions by sulphide of ammonium, the acid by which they were held in solution being neutralised by the ammonia of the reagent, while hydrosulphuric acid escapes.

Certain compounds of the earthy and alkaline-earthy metals with non-volatile acids (phosphates, oxalates, borates, &c.), being soluble in dilute acids and insoluble in water, are similarly precipitated by sulphide of ammonium.

δ. Group 3.—Metals whose *sulphides* and *hydrates* are soluble in water; which, therefore, are not precipitated by hydrosulpuhric acid or sulphide of ammonium from any solution. This group includes the *alkaline-earthy* and *alkaline* metals. They are further subdivided according to their behaviour to carbonate of ammonium in presence of chloride of ammonium.

Subdivision A.—Metals which are precipitated by carbonate of ammonium. They are barium, strontium, calcium. Their normal carbonates are insoluble in water or in chloride of ammonium.

Subdivision B.—Metals which are *not* precipitated by carbonate of ammonium. They are magnesium, potassium, sodium, lithium, ammonium. Carbonate of magnesium is insoluble in water, soluble in chloride of ammonium: the carbonates of the other four metals (alkaline metals), are soluble in water. The different solubility of their phosphates affords a means for the further detection of the metals of this subdivision.

In the usual classification, the alkaline-earthy metals (barium, strontium, calcium, magnesium) constitute Group 3: and Group 4 comprises the alkaline metals.

The following table exhibits in a compendious form the behaviour of all the metals to the general reagents above enumerated.

Behaviour of Metallic Solutions with Hydrochloric Acid, Ammonium,

Hydrochloric Acid.	Hydrosulphuric Acid.		
Metals which are precipitated as *chlorides* from their neutral or acid solutions by *hydrochloric acid.*[*]	Metals which are precipitated as sulphides from their hydrochloric acid solution by *hydrosulphuric acid.*		Metals whose salts are partly *reduced* in an acid solution by *hydrosulph. acid,* with separation of sulphur.[*]
	Soluble in sulphide of ammonium.	*Insoluble in sulphide of ammonium.*	
Lead (partially), white, crystalline, soluble in hot water, precipitated thence by sulphuric acid. **Silver**, white, curdy, soluble in ammonia, precipitated thence by nitric acid. **Mercury as subsalt**, white, finely-divided, blackened by ammonia.	**Arsenic** (yellow). **Antimony** (orange). **Tin**[*] (brown or yellow). **Gold** **Platinum** **[Iridium]** } (black-brown). **Molybdenum**[†] (brown). **[Selenium]** (red-yellow). **[Tellurium]** (black).	**Mercury**[*] **Silver** **Lead**[†] **Copper** } (black). **Cadmium** (yellow). **Bismuth** (brown). **[Palladium]**[‡] **[Osmium]** **[Rhodium]** **[Ruthenium]** } (black-brown).	**Iron as ferric salt.** The solution becomes colourless, and contains a ferrous salt. **Chromium as chromate.** The solution becomes green, and contains a chromic salt.
[*] In a saturated solution of a barium-salt, hydrochl. acid gives a white precip. readily soluble in water. In an *alkaline* solution, hydrochloric (or nitric) acid gives a precipitate in presence of *Silicic* *Boric* *Antimonic* *Tungstic* *Molybdic* *Benzoic* } acids; or of those metals whose oxides are soluble in alkalis (aluminium, &c., soluble in excess of acid); or of *cyanides* and *ferrocyanides*; or of those *sulphides* which are soluble in sulphide of ammonium. In presence of soluble *polysulphides* or *hyposulphites*, sulphur is separated.	[*] SnS is brown, SnS^2 yellow. From the solution of SnS in sulphide of ammonium, hydrochl. acid precipitates yellow SnS^2. [†] The sulphides of *tungsten* and [*vanadium*] are not precip. by hydrosulph. acid from an acid solution: but they are when their solution in sulphide of ammonium is decomposed by an acid.	[*] Mercury as protosalt is precip. white by a little hydrosulph. acid; black by excess. [†] Lead is only precip. completely from dilute, not too acid, solutions. [‡] The sulphides of all the platinum-metals are precipitated very slowly.	[*] Sulphur is also separated in presence of free *chlorine*, *bromine*, and *iodine*, of *sulphurous*, *nitrous*, *hypochlorous*, *chloric*, *iodic*, *bromic acids*, &c.: and generally in presence of easily reducible salts of metals which are not precip. as sulphides from an acid solution.

The metals enclosed thus [ ] are very rare, and

Hydrosulphuric Acid, Sulphide of Ammonium, and Carbonate of successively applied.

Sulphide of Ammonium.			**Carbonate of Ammonium.**	
Metals which are precipitated by *sulphide of ammonium*, in presence of chloride of ammonium. (The solution should be neutralised with ammonia before adding sulphide of ammonium.)			Metals which are precipitated neither by *hydrosulphuric acid* nor by *sulphide of ammonium*. *Carbonate of ammonium*, in presence of chloride of ammonium,	
As Sulphides:	*As Oxides:* also precip. by ammonia.	*As Salts:* also prec. by amm.	*precipitates* [*]	*does not precip.*
Nickel [*] **Cobalt** (black). **Iron** **Uranium** (black-brown). **Manganese** (flesh-red). **Zinc** [†] (white).	a. soluble in potash. **Aluminium** [*] (colour- **[Glucinum]** less). **Chromium** (green). **[Tantalum]** [†]. **[Columbium or Niobium.]** b. insol. in potash. **[Cerium]** **[Lanthanum]** **[Didymium]** generally colourless. **[Yttrium]** **[Erbium]** **[Terbium]** **[Zirconium]** **[Thorium]** **Titanium**	a. in presence of phosphoric acid. **Magnesium** (crystalline). b. in presence of phosphoric, oxalic, boric or hydrofluoric acid. **Calcium** [*] **Strontium** (white). **Barium** as phosphates, oxalates, borates, or fluorides.	**Barium** **Strontium** (white). **Calcium** as carbonates.	a. precipitable by phosphate of ammonium (and ammonia) **Magnesium** (crystalline). b. not precip. by phosphate of ammonium. **Potassium.** **Sodium.** **Lithium.** [*] **Ammonium.**
[*] Sulphides of nickel and cobalt are difficultly soluble in acetic and dilute hydrochl. acids. Sulphide of nickel is slightly sol. in yellow sulphide of ammonium, forming a brown solution. [†] Sulphide of zinc is insoluble in acetic acid.	[*] In presence of phosphoric acid aluminium is also precip. as phosphate, sol. in potash. [†] Soluble after fusion with potash.	[*] The alkaline-earthy phosphates are insol. in potash, sol. in acetic acid. Oxalate of calcium is insol. in acetic acid.	[*] The precipitation is not complete unless ammonia is added, and the whole heated to boiling.	[*] A concentrated solution of a lithium-salt is precip. by phosph. sod. on heating.

need not be sought for except in special cases.

If we suppose the case of a solution containing all the metals, it is obvious that, by the successive application of each of these general reagents, we shall separate, first, by hydrochloric acid, those metals whose chlorides are insoluble; secondly, by hydrosulphuric acid, those metals whose sulphides are insoluble in dilute acids; thirdly, by sulphide of ammonium, those remaining metals whose sulphides or hydrates are insoluble in neutral or alkaline liquids; and lastly, by carbonate of ammonium, those metals whose carbonates are insoluble: so that at last we have only the alkaline metals left in solution. In order, however, to effect the complete separation of each group, the general reagents must be employed *in the order* above stated: for sulphide of ammonium would precipitate those metals whose sulphides are insoluble in dilute acids, as well as those whose sulphides are only insoluble in neutral or alkaline liquids; and carbonate of ammonium, if employed before the other reagents, would precipitate most of the metals of Groups 1 and 2, their carbonates being also insoluble.

The following rules, the importance of which will be obvious on the least reflection, must also be strictly observed.

1. The mineral acid employed to acidify the original solution (when it is not already sufficiently acid), is either hydrochloric or nitric acid. Both are employed dilute, and not in sufficient quantity to interfere with the formation of the sulphides of Group 1. Hydrochloric is generally preferable to nitric acid: for it serves as a general reagent, separating at once those metals which form insoluble chlorides. If nitric acid be employed, these metals will be found in the precipitate by hydrosulphuric acid.

2. The precipitation by each general reagent must be complete. To ensure this, the reagent must be added gradually, allowing the precipitate to subside between each addition, until no further precipitate is produced. In the case of hydrosulphuric acid, the precipitation is complete when the solution, after agitation, still smells strongly of the gas. Gentle heat facilitates the separation of precipitates in almost every case. Arsenic (as arsenic acid), gold, platinum, iridium, rhodium, and molybdenum, are precipitated very slowly by hydrosulphuric acid. Tungsten and vanadium are not precipitated by hydrosulphuric acid from an acid solution: they are, however, included in Group 1, because their sulphides (obtained by adding sulphide of ammonium and then hydrochloric acid), are insoluble in acids, but soluble in sulphide of ammonium.

3. Each group, when precipitated, must be thoroughly freed by washing with water from all members of the subsequent groups, which may be contained in the solution. This washing is effected, according to circumstances, either on a filter, or by decantation. If the precipitate contains any easily oxidable sulphides, a little hydrosulphuric acid must be added to the wash-water (if the sulphide is insoluble in dilute acids, *e.g.* sulphide of copper), or a little sulphide of ammonium (if the sulphide is soluble in dilute acids, *e.g.* sulphides of iron and manganese), in order to prevent the partial oxidation of the sulphide by exposure to the air during the washing of the precipitate. After the precipitation of each group, it is advisable to ascertain the presence or absence of any members of the succeeding groups, by carefully evaporating on platinum-foil a moderate quantity of the filtrate; if, after ignition, there is no distinctly visible residue, non-volatile substances need not be looked for further. It is obvious that, if these two precautions (complete precipitation and thorough washing) be neglected, metals belonging to one group are liable to be found among those of another group; and consequently, as the analysis proceeds, reactions will be obtained which will be the source of great perplexity to the unpractised analyst.

Each group of metals having been separated by the application of general reagents, the presence or absence of each member of each group is ascertained by means of special or characteristic reagents. It seldom happens that the number of elements contained in any inorganic compound exceeds ten or twelve: and in most cases some distinct idea of the nature of its principal constituents is afforded by the results of the preliminary examination. In metallic minerals and alloys, the heavy metals are chiefly to be looked for: in silicates, the earthy, alkaline-earthy, and alkaline metals, iron, and manganese. It frequently happens that important information may be derived from the colour of a precipitate or of a solution. Thus solutions of cupric, chromic, molybdic, and vanadic salts, are blue or green; those of nickel-salts, green; those of ferrous-salts, light bluish-green; those of chromates, gold-salts, ferric- and platinic-salts, yellow, with a red or brown tinge; those of cobalt-salts, red, &c. These colours are not perceptible when the amount of metal present is very small, or when they are masked by the presence of other metals, the colour of whose solutions is complementary to them.

In order to show the systematic method by which the members of each group are detected in presence of each other, we will now briefly go through the most important groups mentioned in the table.

1. *Precipitate produced by hydrochloric acid.*—Chloride of lead is soluble in a large quantity of water, especially on boiling; chloride of silver, in ammonia; subchloride

of mercury is blackened by ammonia. (The addition of either hydrochloric or nitric acid may produce a precipitate in presence of such acids, hydrates, cyanides, sulphides &c., as are soluble in alkaline liquids, but insoluble in water; or a precipitate of sulphur, in presence of a polysulphide or hyposulphite, or a white precipitate, readily soluble in more water, in a saturated solution of a barium-salt.)

2. *Precipitate produced by hydrosulphuric acid.*

a. Portion soluble in alkaline sulphides. — Sulphide of arsenic is soluble in acid sulphite of potassium or in sesquicarbonate of ammonium, the sulphides of antimony and tin are not. When the three sulphides are dissolved in aqua-regia, and the solution is introduced into a Marsh's apparatus, antimony and arsenic are detected by the behaviour of their gaseous hydrogen-compounds; tin, after its separation by zinc, by its solubility in hydrochloric acid, and by the reaction of its solution with chloride of mercury.

b. Portion insoluble in alkaline sulphides. — The precipitate is treated with nitric acid: sulphide of mercury and sulphate of lead may remain undissolved. In the solution, lead is detected by sulphuric acid; silver, by hydrochloric acid; bismuth by its precipitation by ammonia, or by water if no excess of acid is present; copper, by the blue colour of its ammoniacal solution, or by ferrocyanide of potassium; cadmium, by the precipitation of its ammoniacal solution by hydrosulphuric acid, after the addition of cyanide of potassium.

3. *Precipitate produced by sulphide of ammonium.*—The precipitate is digested with excess of caustic potash in the cold: chromium, zinc, aluminium, and glucinum are found in the solution. Of the metals contained in the residue: cobalt, nickel, and manganese form soluble double salts with ammonia, and so are not precipitated by it: iron, uranium, the rarer earthy metals, and alkaline-earthy phosphates, oxalates, &c., are precipitated by ammonia, even in presence of chloride of ammonium. The hydrates of uranium and the rarer earthy metals are readily soluble in carbonate of ammonium: ferric hydrate is less soluble, and the alkaline-earthy salts are insoluble. Ferric salts are detected by sulphocyanate or ferrocyanide of potassium; the alkaline-earthy salts by appropriate characteristic reagents.

4. *Precipitate produced by carbonate of ammonium.* — The metals which compose this group (barium, strontium, calcium) are distinguished by the different solubility of their sulphates, oxalates, chromates, &c.: and by the colours which they communicate to the blowpipe flame, or to that of burning alcohol.

5. The solution, after the successive application of the above general reagents, can only contain magnesium and the alkaline metals. Magnesium is detected by its precipitation by phosphate of ammonium; the alkaline metals by the colour which they impart to the blowpipe or alcohol flame, and by the different solubility of their tartrates or chloroplatinates. Ammonium is always sought for in a separate portion of the original solution: it is detected by the evolution of ammonia when any of its salts are heated with a fixed alkali or alkaline earth.

Since *hyposulphite of sodium* is decomposed by the salts of most of those metals which are precipitated by hydrosulphuric acid from an acid solution, a metallic sulphide being precipitated, it has been proposed to employ this compound as a general reagent instead of hydrosulphuric acid, and so to avoid the unpleasant smell of the latter. This substitution, however, has not as yet been generally adopted.

Carbonate of barium may also be employed as a general reagent. When a solution containing metallic salts is shaken up with excess of this salt, in the cold:

Are precipitated.

Tin.
Gold.
Iridium.
Rhodium.
Palladium.
Platinum.
Mercury.
Copper.
Bismuth.
Cadmium.
Aluminium.
Manganese }
Iron } as sesquisalts.
Uranium }
Chromium, as sesquisalt, or as chromic acid.
Titanium, as titanic acid.

Are not precipitated.

Silver.
Lead.
Iron }
Nickel }
Cobalt } as protosalts.
Manganese }
Zinc.
Cerium.
Yttrium.
Glucinum.
Magnesium.
Calcium.
Barium.
Strontium.
Ammonium.
Lithium.
Sodium.
Potassium.

Mercury, platinum, palladium, rhodium, iridium, and gold are precipitated by carbonate of barium only when they are present as oxygen-salts, not when present as chlorides, &c. Arsenic, antimonic, phosphoric, selenic, and sulphuric acids are not precipitated by carbonate of barium until the solutions of their salts have been acidulated with nitric or hydrochloric acid. Carbonate of barium is not much used as a general reagent; it is however employed with advantage for the separation of the metals which are precipitated by sulphide of ammonium, since it precipitates completely those which are present as sesquisalts, while the protosalts remain in solution.

When, in the course of a systematic qualitative analysis, one or more members of the different groups have been recognised as constituents of the substance under examination, by means of the reactions above enumerated, the results must be confirmed by certain special reactions, which will be detailed at length in the articles devoted to the several elements.

b. *Examination for Acids.*

The qualitative detection of acids, is, on the whole, more difficult than that of metals; still, with due care, it may be accomplished with great precision. In most cases, the preliminary examination, as well as the nature of the metals already found, give information as to what acids should especially be looked for. The knowledge of the solubility of different salts, and of the reactions of their aqueous solutions with vegetable colours, is of the greatest importance in this examination. By heating the substance either alone or with concentrated sulphuric acid, the presence or absence of *organic* and *volatile inorganic* acids is at once ascertained, these acids either volatilising undecomposed, or yielding volatile products of decomposition. For this purpose, a small portion of the dry substance is heated in a test-tube (not to boiling) with 3 to 4 times its volume of concentrated sulphuric acid; when, in the case of all acids which are either volatile without decomposition, or are decomposed by sulphuric acid at a high temperature, gases or vapours are evolved, the properties of which, in most cases, indicate the nature of the acids present.

1. *Non-volatile acids:* whose compounds evolve no vapours when heated with sulphuric acid, the mixture not being blackened—Silicic, Boric, Phosphoric, Sulphuric, Iodic, Arsenic, Selenic, Tungstic, Molybdic, Titanic acids.

2. *Acids which evolve a coloured gas*, the mixture not being blackened—Hydriodic, Hydrobromic, Bromic, Chloric, Hypochlorous, Nitrous acids.

3. *Acids which evolve a colourless gas, generally possesses an irritating smell and an acid reaction*, the mixture not being blackened—*a.* Volatile without decomposition: Hydrosulphuric, Hydrochloric, Nitric, Acetic, Benzoic, Succinic, Hydrofloric acids. The gas evolved is not inflammable, except in the case of hydrosulphuric acid — *b.* Decomposed — Cyanic, Chromic (evolves oxygen), Carbonic, Sulphurous, Hyposulphurous, Polythionic, Oxalic, Formic, Hydrocyanic, Sulphocyanic, acids, Ferro- and Ferri-cyanides. In most of these cases, the gas evolved is inflammable.

4. *Non-volatile organic acids:* Tartaric, Racemic, Citric, Malic, Tannic, Gallic, Uric acids. The mixture is blackened, and carbonic and sulphurous anhydrides and carbonic oxide are evolved.

The behaviour of a mixture of salts, when heated alone or with sulphuric acid, is often different from that of each individual salt under the same circumstances. Thus a mixture of a nitrate or chlorate with a salt of an organic acid, does not blacken when ignited, but commonly detonates: a chloride, in presence of a nitrate, when heated with sulphuric acid, evolves chlorine and red nitrous fumes; in presence of a chromate, red fumes of chlorochromic acid; in a mixture of a sulphite and a nitrate, chlorate, chromate, &c., the sulphurous acid is converted into sulphuric acid; in a mixture of a sulphide and a sulphite, the two acids decompose each other, sulphur being separated, and the characteristic smell of each destroyed. Chloride and subchloride of mercury, and chloride of tin are decomposed with difficulty, if at all, by sulphuric acid.

From a solution containing volatile and non-volatile acids, the former may be separated by distillation with dilute sulphuric acid.

The general reagents usually employed in the examination for acids in the wet way, are chloride or nitrate of barium; chloride of calcium; a mixture of sulphate of magnesium, ammonia, and chloride of ammonium; sesquichloride of iron; nitrate of silver; and indigo-solution. By these reagents, the most important acids are divided into the following groups.

1. Acids which are precipitated by *chloride of barium:* —

a. from a solution acidulated with nitric or hydrochloric acid—Sulphuric, Selenic, Fluosilicic acids.

b. From a neutral solution (the precipitate being soluble in acids) — Sulphurous, Phosphoric, Carbonic, Silicic, Hydrofluoric, Oxalic, Chromic, Boric, Tartaric, Citric, Arsenious, Arsenic acids. The last five acids are not precipitated in presence of ammoniacal-salts.

2. Acids which are precipitated by *chloride of calcium:* —

a. From a neutral solution only (the precipitate being soluble in acetic acid)—Phosphoric, Arsenic, Boric, Carbonic, Sulphurous, Tartaric, Citric acids, and Ferrocyanides.

b. From a neutral or acetic acid solution—Sulphuric, Hydrofluoric, Oxalic, Racemic acids.

3. Acids which are precipitated by *sulphate of magnesium, in presence of ammonia and chloride of ammonium*—Phosphoric, Arsenic, Tartaric acids.

4. Acids which are detected by *sesquichloride of iron:* —

a. Are precipitated — Ferrocyanides (from a solution containing free hydrochloric acid): Phosphoric, Arsenic, Tannic acids (from a neutral or acetic acid solution): Boric, Benzoic, Succinic acids (from neutral solutions only).

b. Are coloured — In presence of free hydrochloric acid; Ferricyanides (brown), Sulphocyanic acid (red). In neutral solutions only: Acetic, Formic, Sulphurous, Meconic acids (red): Gallic acid (black).

5. Acids which are precipitated by *nitrate of silver:* —

a. From neutral solutions only (precipitate being soluble in dilute nitric acid) — Phosphoric, Pyro- and Meta-phosphoric, Arsenic, Arsenious, Chromic, Oxalic, Boric, Tartaric, Citric, Sulphurous, Formic acids: Silicic and Acetic acids from concentrated solutions.

b. From acid solutions also (the precipitate being insoluble in dilute nitric acid). Hydrochloric, Hydrobromic, Hydriodic, Hydrocyanic, Sulphocyanic, Iodic, Hydrosulphuric acids, and Ferro- and Ferri-cyanides.

6. *Indigo-solution* is decolorised, without the addition of an acid, by free chlorine and bromine; by all the oxygen-acids of chlorine, when free, and by metallic hypochlorites; by free nitric acid, if not too dilute, by alkaline sulphides, and by caustic alkalis. On addition of sulphuric acid, and heating, by chlorates, bromates, iodates, and nitrates. On addition of hydrochloric acid, and heating (chlorine being evolved), by all the foregoing compounds; also by chromates, selenates, tellurates, vanadates, manganates, permanganates, ferrates, and all peroxides.

In investigating the acids contained in a soluble compound, the first step is to ascertain the behaviour of the solution to vegetable colours. When, as is frequently the case, a neutral solution is required, the solution, if acid, is neutralised by ammonia: if alkaline, by nitric acid, or, if nitrate of silver be not employed as a reagent, by hydrochloric acid. But, as many of the heavy metals, as well as some alkaline-earthy salts, are precipitated when their solution is neutralised by ammonia, it is generally necessary to remove from the solution all metals except the alkaline metals, before proceeding to test for acids; in which process, the presence or absence of metallic acids, and of alkaline-earthy phosphates, oxalates, &c. will be ascertained. When this is not done, it is frequently necessary to substitute for the general reagents mentioned above, the nitrate of the same base, since nitric acid forms no insoluble salts: thus nitrate, instead of chloride, of barium, must be employed in solutions containing lead, silver, or subsalts of mercury. We have already mentioned cases in which the addition of nitric or hydrochloric acid to an alkaline solution will produce a precipitate. The following acids are also precipitated by the mere acidulation of their alkaline solutions: Tungstic, Molybdic, Antimonic, Benzoic, Uric acids; Boric and Silicic acids from concentrated solutions. Under the same circumstances, a precipitate of sulphur is produced in presence of hyposulphurous acid or polysulphides: of iodine, in a solution containing an iodide and an iodate: of acid tartrate of potassium or ammonium, in a solution containing the normal tartrates of these metals. The nature of the metals found in a solution will often imply the absence of one or more acids: generally speaking, a neutral or acid solution containing one of the metals whose salts are used as general reagents for acids, need not be examined for any of those acids which are precipitated by that metal. Thus, sulphuric or hydrochloric acid need not be sought for in soluble compounds containing barium or silver respectively. In order not to overlook the presence of uncombined volatile organic acids, the acid solution is neutralised with carbonate of sodium, evaporated to dryness, and ignited: when the organic acid, which, if free, would have been volatilised undecomposed, is decomposed, with separation of carbon.

Substances which are insoluble in water or acids are rendered soluble by one of the methods already described, and the solution is examined for acids in the wet way. Insoluble compounds of the heavy metals are mostly decomposed by digestion with sulphide of ammonium; sulphates of strontium and calcium by digestion with carbonate of sodium: in both cases, the filtrate contains the acid, together with an excess of the decomposing agent, while the metal is found in the residue. Insoluble salts of organic acids are decomposed by boiling with an alkaline carbonate; ferric salts of volatile organic acids by digestion with ammonia: in both cases, the filtrate contains an alkaline salt of the acid. Sulphides and all salts of the lower oxygen-acids of sulphur, yield sulphuric acid when digested with nitric acid, or any other oxidising agent.

The application of confirmatory tests is as necessary in the case of acids as in that of metals.—F. T. C.

The methods of *quantitative inorganic analysis* cannot be included in one article. The processes for the separation and quantitative estimation of each element are described in the article devoted to that element. The analysis of ashes, soils, mineral-waters, &c. and volumetric analysis, are also described in separate articles. We may here however describe a method, of general application, which is found useful in many cases, viz.:

The Indirect method of Quantitative Analysis.—The usual method of determining the quantities of the several constituents of a compound or mixture, is to separate each of them in the form of a definite compound, which can be collected and weighed, *e. g.* silver as chloride, barium as sulphate, &c., and calculate the weight of the required constituent from the known composition of this compound. It sometimes happens however, that the complete separation of certain substances is very difficult, or even impossible, and in that case, recourse is had to a method of determination, which depends on the general principle that any number of unknown quantities may be determined simultaneously, if we can find between them a number of relations equal to that of the quantities themselves; in other words, n unknown quantities may be determined by means of n equations.

Suppose for example, we have a mixture, either solid or liquid, containing potassium and sodium, in the form of hydrates or carbonates. Take two equal portions of the mixture (it is not necessary to know the weight of these portions), convert one portion into chlorides, the other into sulphates, and weigh the two products. Let the sum of the weights of the chlorides be a, and that of the sulphates b: the unknown weight of potassium x, and that of sodium y; then from the known atomic weights of the metals, their chlorides and sulphates, we have:

$$\frac{74\cdot5}{39}x + \frac{58\cdot5}{23}y = a$$

$$\frac{87}{39}x + \frac{71}{23}y = b$$

whence the quantities x and y may be determined.

Another form in which the indirect method may be applied to the determination of two substances, is to bring them both together into a form in which they can be weighed, *e. g.* as chlorides or sulphates, and determine the quantity of chlorine or of sulphuric acid in the mixture; thus, suppose a mixture of potash and soda to be converted into chlorides: let the sum of the weights of these chlorides be s, and let the amount of chlorine in this mixture, determined as chloride of silver, be c; then if x be the quantity of potassium and y the quantity of sodium, we have the two equations:

$$\frac{\mathrm{KCl}}{\mathrm{K}}x + \frac{\mathrm{NaCl}}{\mathrm{Na}}y = s; \qquad \frac{\mathrm{Cl}}{\mathrm{K}}x + \frac{\mathrm{Cl}}{\mathrm{Na}}y = c$$

$$\text{or} \qquad \frac{74\cdot5}{39}x + \frac{38\cdot5}{23}y = s; \qquad \frac{35\cdot5}{39}x + \frac{35\cdot4}{23}y = s$$

whence x and y may be found.

If three substances are to be determined, *e. g.* barium, strontium, and calcium, we should of course require three equations, which, in the case supposed, might be obtained by weighing the three substances, first as carbonates, then as oxalates, then as sulphates. It is seldom, however, that the indirect method is applied to the determination of more than two substances.

A case in which this indirect method of analysis is often applied, is to the determination of a small quantity of bromine or iodine in presence of chlorine, as in the analysis of mineral waters. The chlorine and bromine are precipitated by a solution of silver, and the mixed chloride and bromide of silver is weighed. It is then ignited in a stream of chlorine till all the bromine is expelled, and the resulting chloride is again weighed: let the difference of the two weights be d: then, since chlorine and bromine replace one another in the proportion of their atomic weights, viz. as 35·5 to 80, we have:

$$\mathrm{Br} - \mathrm{Cl} = d; \qquad \frac{\mathrm{Br}}{\mathrm{Cl}} = \frac{80}{35 \cdot 5}$$

whence $\mathrm{Br} - \frac{35 \cdot 5}{80} \mathrm{Br} = d; \qquad \frac{44 \cdot 5}{80} \mathrm{Br} = d.$

and therefore $\mathrm{Br} = 1 \cdot 797\, d.$

The indirect method of analysis can only be employed with advantage to ascertain the relative quantities of substances whose atomic weights differ considerably: with a mixture of bodies of the same atomic weight, it cannot give any definite result; in fact the two equations which it involves become in that case identical.

ANALYSIS (ORGANIC).—The analysis of organic substances divides itself, like that of inorganic bodies, into qualitative and quantitative. A further division is also convenient, viz. into *Elementary* or *Ultimate Analysis* and *Proximate analysis*, according as the object of the inquiry is to determine the ultimate elements, carbon, hydrogen, &c., of which the body is composed, or the proximate principles, such as sugar, starch, fibrin, &c., in which those elements are grouped.

I. ELEMENTARY OR ULTIMATE ORGANIC ANALYSIS.

Organic bodies are composed of carbon, hydrogen, and oxygen, with or without nitrogen, sometimes also associated with sulphur and phosphorus: these are all the elements that occur in natural organic compounds; those which are artificially prepared may contain any elements whatever.

The detection and estimation of these elements depends essentially on the process of COMBUSTION. When an organic compound is heated to redness in contact with free oxygen, or with a substance which gives up that element with facility, it is completely decomposed, its elements being separated either in the free state or in new forms of combination.

Qualitative Analysis. *Carbon* and *Hydrogen* are detected by burning the compound in a glass tube in contact with oxide of copper or chromate of lead. The carbon is then converted into carbonic acid*, which if passed into baryta-water, forms a white precipitate of carbonate of barium, and the hydrogen into water, which collects in drops in a small cooled receiver attached to the combustion-tube, or, if in very small quantity, may be rendered visible by causing the vapour to pass through a narrow glass tube lined with phosphoric anhydride, which if water is present, will be converted into phosphoric acid and dissolved. Carbon may also, in nearly all cases, be detected by the black residue which remains when the organic substance is burned in the air, or ignited in a close vessel, or heated with strong sulphuric acid; very few organic bodies contain sufficient oxygen to burn away the carbon completely, even in contact with the air. The black residue of carbonaceous matter may be distinguished from black substances of inorganic origin, by burning slowly away when heated to redness, and by its property of deflagrating with nitre and chlorate of potassium.

Nitrogen in organic bodies is for the most part given off in the free state when the compound is burned with oxide of copper, but a surer mode of detecting it, especially when in small quantity, is to heat the substance in a test-tube with a considerable excess of hydrate of potassium or sodium. The carbon is then converted into carbonic acid by the oxygen of the alkaline hydrate, while the whole or the greater part of the hydrogen unites with the nitrogen to form ammonia, which may be detected by its odour, by its action on litmus paper, and by the white fumes which it produces when a glass rod dipped in dilute hydrochloric acid is held over the mouth of the tube (see AMMONIA). A still more delicate test for nitrogen is the following, given by Lassaigne. A portion of the organic compound is fused in a test-tube with a small piece of potassium; the mass is treated with water when cold; and the liquid boiled with protosulphate of iron partially oxidised by contact with the air. If it be then supersaturated with hydrochloric acid, the presence of nitrogen will be indicated by the formation of a precipitate of Prussian blue, or in case of very minute quantities, by a bluish green colour being communicated to the solution.

Chlorine in organic bodies is detected by igniting the compound with quick lime, whereby it is completely destroyed, the chlorine uniting with the calcium, in which state of combination it may be dissolved out by water, and the chlorine precipitated by nitrate of silver. In some organic compounds which contain hydrochloric acid ready formed, viz. the hydrochlorates of the organic bases, the chlorine may be immediately detected by nitrate of silver without this preliminary treatment.

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* Throughout this article, the term *carbonic acid* is used for CO^2, in accordance with established usage, instead of the more correct appellation *carbonic anhydride*.

Bromine and *Iodine* may be detected by similar treatment; *Fluorine* in the same manner as in inorganic bodies.

Sulphur, *Phosphorus*, and *Arsenic*, are detected by igniting the organic compound with a mixture of hydrate of potassium, and nitre or chlorate of potassium, whereby those elements are converted into sulphuric, phosphoric, and arsenic acids, the presence of which may be demonstrated by reactions appropriate to each.

Metals occurring in organic compounds, remain for the most in the form of oxides, or in the metallic state when the organic matter is burnt. Mercury may be detected in the ordinary way, by distillation with lime.

Quantitative Analysis. The first quantitative analyses of organic bodies were made by Gay-Lussac and Thénard. The substance to be analysed was mixed with a known weight of *chlorate of potassium*, and made up into small pellets, which were dropped one by one through a stopcock of peculiar construction, into an upright glass tube heated to redness, the gas thereby produced escaping by a lateral tube and being collected over mercury. The volume of gas was exactly measured, and the carbonic acid absorbed by caustic potash. The remaining gas consisted either of pure oxygen, or (in the case of azotised bodies) of a mixture of oxygen and nitrogen, the proportions of which were determined eudiometrically (see ANALYSIS OF GASES). Knowing then the weight of the substance burned, the weight of the chlorate of potassium used, and consequently the quantity of oxygen evolved, also the quantity of carbonic acid produced, and of the oxygen remaining after its absorption, sufficient data were obtained for calculating the amount of carbon, hydrogen, and oxygen in the substance analysed: for, the difference between the total quantity of oxygen which had disappeared, and that which was consumed in burning the carbon (this latter quantity being equal in volume to the carbonic acid produced), gave the quantity which had united with the hydrogen to form water, and thence the amount of hydrogen was calculated.

This process was a great step in chemical science, and yielded many important results; but it was difficult of execution, requiring great skill on the part of the operator; it was also inexact in the case of nitrogenous bodies, and totally inapplicable to liquid or volatile compounds. Berzelius simplified it by mixing the chlorate of potassium with common salt, thereby causing the combustion to go on gradually, and rendering it possible to introduce the whole of the material at once. He also collected and weighed the water produced, and thus greatly simplified the calculation.

Saussure and Prout burned the organic substance in an atmosphere of oxygen. Prout's apparatus was so contrived that the substance was burnt in a measured volume of oxygen, and the volume of the gas remaining after combustion was compared with the original volume. Now, since the volume of carbonic acid produced by the combustion of carbon is equal to that of the oxygen consumed, while that which unites with the hydrogen to form water disappears altogether, it follows that if the organic substance contains oxygen and hydrogen exactly in the proportion to form water (as in acetic acid, sugar, &c.), the volume of gas remaining after combustion will be equal to that of the original oxygen: whereas if the proportion of hydrogen is greater (as in alcohol and ether), the volume of gas will be diminished by the combustion; and if the proportion of hydrogen is less (as in oxalic acid), the volume of gas will be increased. Hence, by absorbing the carbonic acid with potash and measuring the residual gas, sufficient data were obtained for calculating the quantities of carbon, hydrogen, and oxygen.

The method now universally adopted for the estimation of carbon and hydrogen in organic compounds, consists in burning the compound with a large excess of oxide of copper or chromate of lead, and determining the quantities of carbonic acid and water produced by the combustion, not by measure but by weight, the water being absorbed by chloride of calcium, and the carbonic acid by potash. The use of oxide of copper was first introduced by Gay-Lussac and afterwards adopted by Ure; but it is to Liebig that we are indebted for those modifications of the process which have brought it to its present state of simplicity and exactness.

The process, as now performed, requires the following materials and apparatus.

Oxide of Copper.—Prepared by dissolving copper in nitric acid, evaporating to dryness, and calcining the residual nitrate in a crucible at a low red heat. As thus prepared, it is a dense, soft black powder, which rapidly absorbs water from the air even before it is quite cold. If, however, it be very strongly heated, it aggregates into dense hard lumps, which, when broken into small pieces and sifted from the finer powder, yield an oxide well adapted for the combustion of volatile liquids. Oxide of copper may also be prepared by igniting copper turnings in a muffle. The oxide thus obtained is much harder and less hygroscopic than that prepared from the nitrate, but it is not so easily mixed with an organic substance in the state of fine powder. Oxide of copper must always be heated to low redness immediately before use.

Chromate of Lead.—Prepared by precipitating a solution of acetate of lead with bichromate of potassium, fusing the washed and dried precipitate in a crucible, and pulverising it in an iron mortar; it is then obtained in the form of a yellow-brown powder. It is but very slightly hygroscopic; but to ensure its complete dryness, it should be preserved in stoppered bottles and heated over a lamp just before it is used.

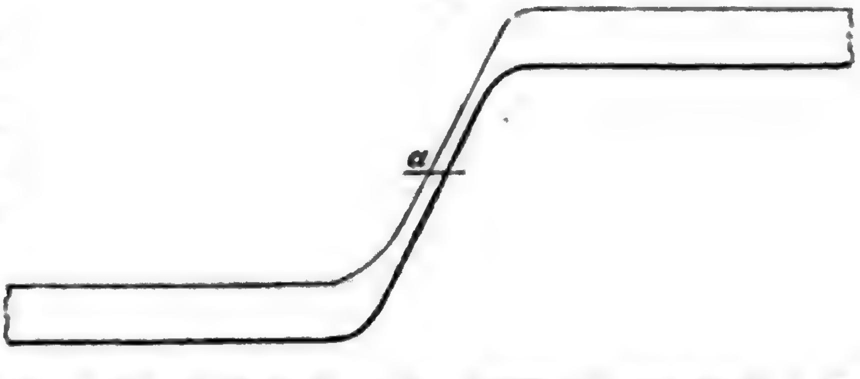
Metallic Copper.—Used in the analysis of bodies containing nitrogen. The most convenient form is that of fine copper turnings, or thin foil rolled up into a spiral. As the surface, especially of the turnings, is seldom clean, the metal should first be heated in a current of air, to destroy any organic matter adhering to it, then pressed into a combustion-tube, and heated in a current of dry hydrogen gas to reduce the oxide previously formed, the heat being continued as long as vapour of water continues to be given off, and the stream of hydrogen afterwards kept up till the metal is cold. By this treatment, the surface becomes covered with finely divided copper, which is very hygroscopic and must therefore be strongly heated over a lamp before use. Finely divided copper reduced by hydrogen from the oxide, is not applicable, being found to decompose carbonic acid at a red heat.

Combustion-tubes of hard glass.—They must be capable of sustaining a strong red heat without melting or even softening to such a degree as to be blown out by the pressure of the evolved gases. The best are made of the hard Bohemian glass (silicate of calcium and potassium), which may now be procured without difficulty. Glass containing lead is utterly unfit for the purpose. When the temperature required for a combustion is very high, the tube should be protected by wrapping it in copper foil or brass wire-gauze, to prevent it from bending if it becomes softened by the heat.

The length and diameter of tube required vary according to the substance to be burnt. For the combustion of ordinary solids, tubes of half an inch internal diameter, and 18 inches long, are well adapted: for solids containing very little carbon, a diameter of $\frac{4}{10}$ of an inch is sufficient: for liquids, it is necessary to use tubes $\frac{6}{10}$ of an inch wide and 20 or 30 inches long, the length being greater as the liquid is more volatile. The use of tubes of larger dimensions than the particular case requires, is not to be recommended, as it involves waste of oxide of copper and increases the unavoidable errors of the operation.

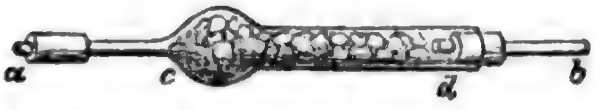
The tubes, after being thoroughly cleansed and dried, are drawn out into an inclined neck, and sealed at one end, while the other end is cut as evenly as possible with a file, and afterwards made smooth at the edges by careful heating in the blowpipe flame. The best mode of sealing is to take a tube of double the length required, soften it in the middle by means of a powerful blowpipe flame, then draw it out in the manner shown in *fig.* 8, and apply the point of the flame for an instant at the middle of the neck *a*, so as to divide and seal it. By this means, two tubes of the required shape are made at once.

Fig. 8.



Chloride of calcium tubes.—The chloride of calcium for absorbing the water generated in the combustion, is usually contained in a bulb-tube of the form shown in *fig.* 9. The end *a* passes through a perforated cork fitting into the combustion-tube, and the end *b* is fitted with a cork and narrow glass tube, which is connected with the potash-apparatus by means of a flexible tube of caoutchouc. Small plugs of cotton-wool are placed at *c*, *d*, to keep the chloride of calcium in its place. The cork *d* should be covered with sealing wax, so that it may not vary in weight by loss or absorption of atmospheric moisture.

Fig. 9.

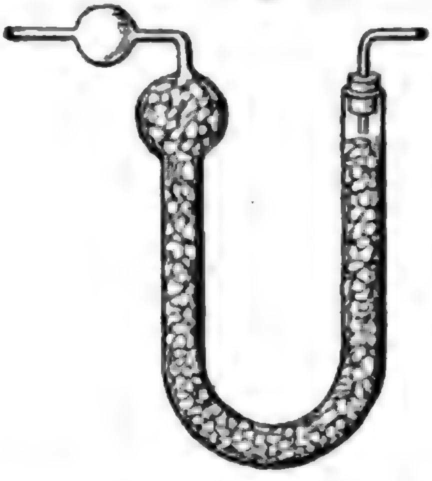


Another form of this apparatus presenting some advantages is the U-tube (*fig.* 10) having at the end nearest to the combustion-tube, a small test-tube, *t*, which serves to collect the greater part of the water, so that the chloride of calcium does not get so much wetted, and may be used several times without renewal. Chloride of calcium tubes are sometimes also made in the form of a U-tube (*fig.* 11), having two bulbs, the one at the extremity of the arm of the tube being filled with chloride of calcium, and the upper being empty to receive the greater part of the water. This form of tube is more expensive than that last described (*fig.* 10), and does not appear to possess any advantage over it.

The U-tube must always be used in preference to the straight tube (*fig.* 8), when the combustion is made in a stream of oxygen gas; because the current of gas being then rather strong, is apt to carry the vapour of water through the straight tube so quickly that a portion of it escapes uncondensed, whereas the U-tube detains it longer, and is more likely to ensure complete absorption.

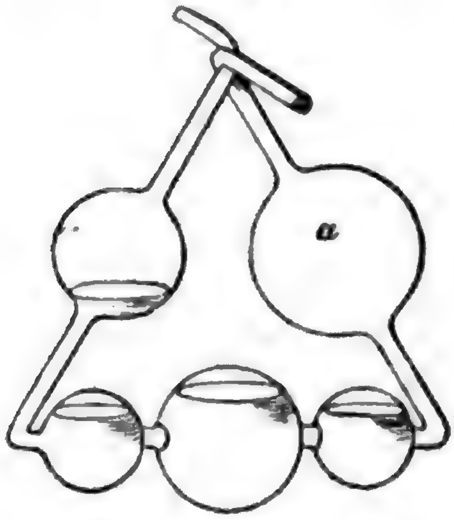
Fig. 10.

Fig. 11.



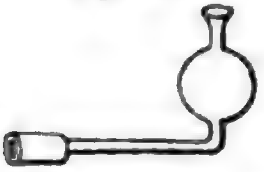
The chloride of calcium should be in the spongy state in which it is obtained by drying at about 200° C. The fused chloride is not so good for the purpose, because it often contains free lime, which absorbs carbonic acid as well as water.

Fig. 12.



Potash-bulbs. — The solution of caustic potash which absorbs the carbonic acid, is contained in a Liebig's bulb-apparatus (*fig.* 12), the form of which is so contrived as to keep the bubbles of gas in contact with the solution for a considerable time, without using a long column of liquid. The large bulb *a*, is connected with the chloride-of-calcium tube, the other extremity of the apparatus being left open. The solution of potash should have a density of about 1·27. If a weaker ley be used, the carbonic acid will not be completely absorbed, and stronger ley is apt to froth, and in that case a portion of it is sure to be forced out at the open end of the apparatus, thereby annihilating the result of the experiment. To fill the bulbs, the potash solution is poured into a small beaker or crucible, and drawn into the apparatus by means of a small suction-tube (*fig.* 13), attached to one end by means of a perforated cork. The quantity of liquid introduced should be sufficient to nearly fill the three lower bulbs, not more: the apparatus thus filled weighs from 40 to 50 grammes. Before weighing, it must be carefully wiped on the outside; and the inside of the tube, by which the liquid has entered, must be dried by means of a thin roll of filtering paper.

Fig. 13.



Corks.—The connection between the combustion-tube and the chloride of calcium tube, is made by a perforated cork. The greatest pains should be taken to select for the purpose good corks, smooth, and free from flaws. They should be softened by beating or by pressure. Immediately before the combustion, the cork must be thoroughly dried in an air-bath or sand-bath at a temperature a little above 100° C.: too great a heat must be avoided, as it renders the cork brittle.

Caoutchouc-tubes. — The chloride-of-calcium tube is connected with the potash-apparatus by a flexible tube of caoutchouc. These tubes are easily made by binding a piece of sheet-caoutchouc over a glass rod or tube of the proper size, and cutting it with a single stroke of a pair of scissors. If the edges be then pressed together, a perfectly tight tube will be made. The connections are made air-tight by tying with silk cord. Tubes of vulcanised caoutchouc, which may be purchased ready made, may also be used, and if of such a size as to require some force to fit them to the tubes, they make an air-tight joint without tying; they must however always be previously digested with a moderately strong solution of potash, in order to remove the sulphur, which is otherwise apt to get into the chloride of calcium tube and potash-apparatus.

Combustion-furnaces.—The combustion-tubes are heated either with charcoal or with coal gas: formerly charcoal was the only fuel employed; but gas-furnaces are now coming into general use. Furnaces have also been constructed for burning spirit; but the high price of that material in most countries renders its use very limited.

The charcoal-furnace is made of sheet iron, in the form of a trough (*fig.* 14), 22 to 24 inches long, and 3 inches high. The bottom is 3 inches wide, wth narrow apertures about $\frac{1}{2}$ an inch apart, which form a sort of grate; the sides of the furnace are inclined outwards, and $4\frac{1}{2}$ inches apart at top. To support the combustion-tube, pieces of strong sheet-iron of the form D (*fig.* 15), are riveted to the bottom of the furnace at intervals; they are of exactly equal height, with their edges ground flat, and correspond with the round aperture in front of the furnace A. The furnace is placed upon flat bricks, so that but little air can enter the grating unless the whole is purposely raised; the draught can thus be regulated at pleasure. The heat produced by the charcoal fire is very regular, and may be raised to any degree required, higher indeed than the best combustion-tubes can bear; on the other hand, the use of charcoal as fuel has many inconveniences; the operator is exposed to great heat and to the deleterious fumes of carbonic oxide, and the ash flies about to such an extent that it is always necessary to perform the combustions in a room apart from the general laboratory.

Fig. 14.

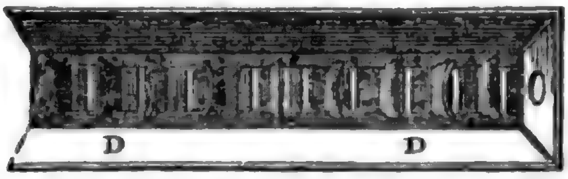
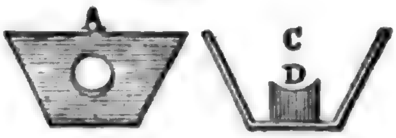


Fig. 15.



For these reasons, it has long been considered desirable to use coal-gas as the fuel for the combustion process, and several forms of furnace have been contrived for the purpose. It is only lately, however, that the problem has received a satisfactory solution, viz. in the gas furnace constructed by Dr. Hofmann, and described by him in the Journal of the Chemical Society, vol. xi. p. 30, whence the following details and illustrations are taken.

In using coal-gas as fuel, it is essential that the gas while burning be mixed with air in sufficient quantity to ensure complete combustion and prevent smoking. This is usually effected by interposing a sheet of wire gauze between the flame and the orifices from which the gas issues. This contrivance was indeed adopted in a form of furnace for organic analysis invented some years ago by Dr. Hofmann, and has also been adopted by others. But all furnaces thus constructed are very liable to get out of order, in consequence of the speedy destruction of the wire gauze; moreover, they do not afford sufficient heat for many combustions: hence they have not come into general use.

In the new form of gas furnace, the mixing of the gas with air is attained by causing it to issue through a number of small orifices placed very close together. For this purpose, a peculiar form of burner is used, called *atmopyre* (*fig.* 16). It consists of a hollow cylinder of burnt clay, closed at top, open at bottom, and having numerous perforations in the sides. Those which are used for the combustion-furnace, are 3 inches high, $\frac{7}{8}$ of an inch in external, and $\frac{3}{8}$ internal diameter. The perforations, of about the thickness of a pin, are made in rows, each cylinder having 10 rows of 15 holes each. From such a clay cylinder loosely fixed upon an ordinary bat's wing burner, the stopcock of which has been properly adjusted, the gas burns with a perfectly blue smokeless flame, which envelopes the cylinder and soon renders it incandescent.

Fig. 16.

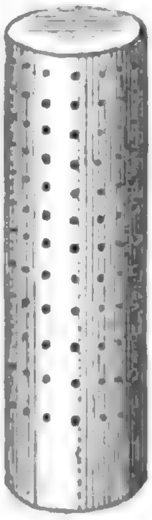
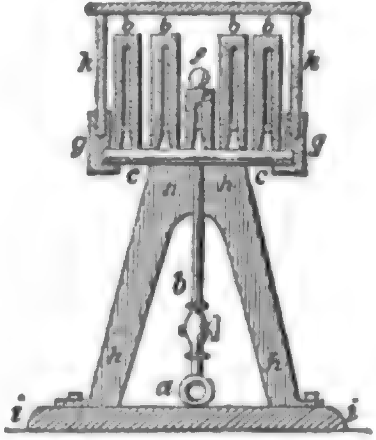


Fig. 17.

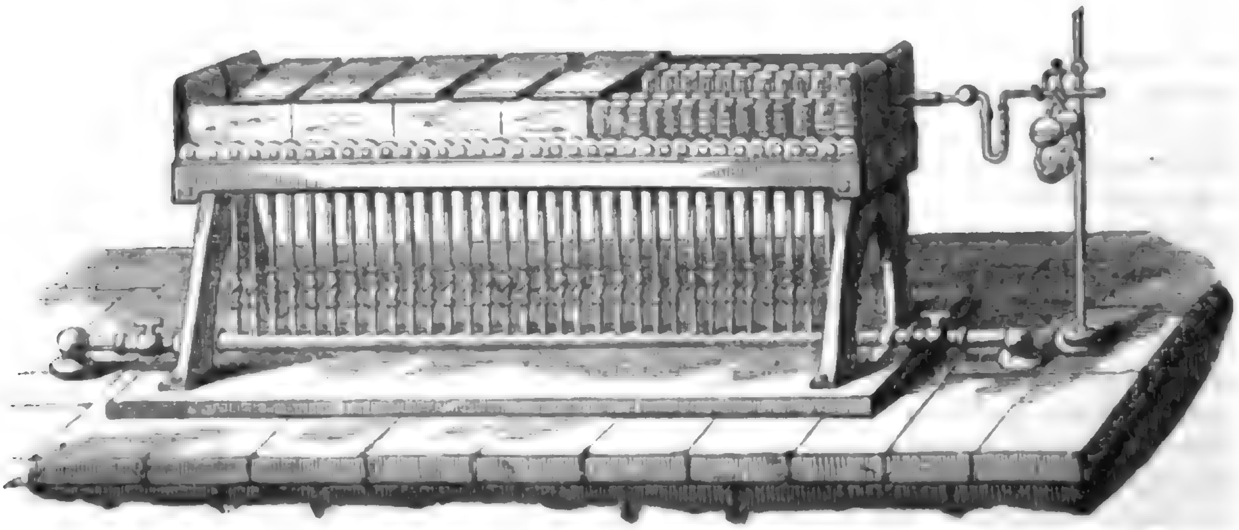


a. Horizontal gas pipe.
b. Vertical gas pipe provided with stop cock.
c c. Brackets for burners.
d d d d. High clay burners.
e. Low clay burners.
f. Combustion tube.
g g. Wrought iron frame.
h h. Cast iron supports.
i i. Cast iron footplate.
k k. Sides of fire-clay.
l l. Cover plates of fire-clay.

The disposition of the apparatus is shown in *fig.* 17. Into a brass tube *a*, from 3 feet to 3 feet 8 inches long, and 1 inch in diameter (shown in section in the figure), which communicates at both ends with the gas-main of the laboratory, there are screwed from 24 to 34 tubes *b*. These tubes, $\frac{1}{2}$ an inch wide and 7 inches high, are provided with stopcocks and carry brackets *c c*, $\frac{1}{2}$ an inch long, and $\frac{5}{8}$ of an inch in diameter, for the reception of five ordinary bat's wing burners (each consuming from 3 to 4 cubic feet of gas per hour, for a full luminous effect) upon which are fixed a corresponding number of clay burners. These clay burners *d d d d*, have the dimensions above stated, excepting the middle one, which is only $1\frac{7}{8}$ inches high and has 70 or 80 perforations. It serves as a support for the combustion-tube *f*, which is thus bedded in a channel of heated fire-clay. The system of brackets lying side by side, acquires sufficient stability by a strong iron frame *g g*, which rests upon two firm supports *h h*, of cast-iron, fastened down by screws upon the foot-plate, *i i*, likewise of cast-iron. The iron frame *g g*, has moreover a groove for the reception of moveable side plates of fire-clay *k k*. They are of the same height as the high burners, over which they project about $\frac{5}{8}$ of an inch, in consequence of their resting upon the frame *g*; lastly, *l l* are covering plates, likewise of fire-clay, which are supported by the side plates *k k*.

The whole disposition of this apparatus will be best understood by the perspective view given in *fig.* 18. In the front part, contiguous to the potash-apparatus, the side plates and the covering plates are omitted, in order to show the disposition of the burners. During the combustion, however, all the burners are inclosed, as exhibited in the posterior part of the apparatus.

Fig. 18.



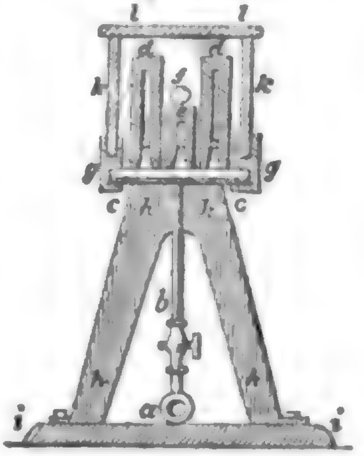
The efficiency of the furnace depends essentially upon the correct disposition of the gas jets. The most appropriate space between the several burners, is about $\frac{1}{8}$ inch. It is very important for the attainment of a perfectly uniform temperature that the several brackets bearing the burners should be equidistant. Their position is therefore specially secured by every bracket being fixed in an aperture formed in the iron frame *gg*, *fig.* 17.

According to the length of the combustion-tube, from 8 to 10 stopcocks (under all circumstances the largest possible number) are opened at once at the commencement of a combustion. If care has been taken to regulate the amount of gas, either by the stopcocks in the horizontal gas pipe, or by those in the separate supply-tubes, the lighted portion of the furnace will, in 10 or 12 minutes, be in a state of perfect incandescence. After this it is only necessary to open the remainder of the stopcocks, in appropriate succession, to insure a slow and regularly progressing combustion. The time required for the completion of an analysis varies from 40 minutes to an hour, rarely more.

The heat obtained by this furnace is very regular; and since it is conveyed to the combustion-tube chiefly by radiation from the incandescent mass of surrounding clay every part of the tube is equally heated. The temperature which it is capable of yielding *is entirely* at the command of the operator. When strained to its full power, it gives a heat equal to that of the strongest charcoal combustion-furnace; but by properly adjusting the stopcocks, it may be kept at any desired temperature, especially since it is only necessary to look into the channel, when, with a little practice, a correct idea of the temperature is rapidly obained from the colour of the glowing cylinders. It deserves, however, to be noticed that the apparatus furnishes rather more heat than is generally required; it is preferable, therefore, under all circumstances, to protect the combustion-tube by a metallic shield: for this purpose ordinary brass wire gauze may be conveniently employed; it is more easily manipulated, and may be used longer than the thin copper or brass plate generally employed.

One great advantage of this furnace is its durability. The clay plates and burners show but little tendency to split, and the mixture of gas and air is so perfect that the holes in the burners never become stopped up with carbon. Moreover, the cost of the gas consumed is very much less than that of the charcoal required to produce the same amount of heating effect. Dr. Hofmann has found that a combustion lasting 1 hour, and requiring the whole length of the furnace (34 rows of burners), consumes from 80 to 90 cubic feet of gas. For a carbon determination, with 24 rows of burners, which generally lasts about 40 minutes, from 50 to 60 cubic feet are required, and for a nitrogen determination, 25 to 30 cubic feet. In laboratories where many combustions are made, the saving of fuel soon covers the original cost of the furnace.

Fig. 19.



The expense of the apparatus and the consumption of gas, may be diminished by reducing the number of rows of burners from 5 to 3, as shown in *fig.* 19. The heat given by such a furnace is of course not so great as that afforded by the larger one, but it is sufficient for nearly all combustions.

Several other forms of gas furnace for organic analysis have also been proposed. One of these invented by Babo, which is much used in the German laboratories, is represented in *fig.* 26, page 235.

Preparation of the Substance for Analysis.

Before proceeding to determine the proportion of the elements in an organic compound, it is necessary to ensure that the substance is in a perfectly pure and definite state. It is but seldom that the processes of ultimate analysis can be advantageously applied to complex organic mixtures; only indeed when the proportion of a single element is to be determined for commercial purposes, as in the valuation of articles of food or of manures by the quantity of nitrogen which they contain.

In solids, uniformity and regularity of structure, whether crystalline or otherwise, is in many cases the best test of purity: in such cases, examination by the microscope is often of great service. Constancy of melting-point is also a test of the purity of many substances, especially of fatty bodies. The purification of solids is generally effected by recrystallisation from solution, or from the fused state, or in the case of volatile bodies, by sublimation. In liquids, the chief test of purity is constancy of boiling point, and purification is effected chiefly by fractional distillation. In all cases a small quantity of the substance must be burnt upon platinum foil, in order to ascertain whether it contains any inorganic matter; if the organic body is pure, it will burn without residue. If inorganic matter is present in considerable quantity, or if it forms an essential part of the compound, as in the salts of organic acids, its quantity must be exactly determined by burning a weighed portion of the compound.

Further, it is necessary before proceeding to the process of combustion, to free the compound from hygroscopic water. For this purpose, a weighed quantity of the substance is heated for some time in a water-bath at 100°, and then weighed again; if it has lost weight, it is again heated and again weighed: and these operations are repeated till two successive weighings, between which the substance has been heated, give the same result. The substance may then be considered dry.

Bodies which cannot bear a temperature of 100° C. without decomposition, may be dried by placing them over a large dish containing strong sulphuric acid, and covering the whole arrangement with a bell-jar; the desiccation is greatly accelerated by placing the whole apparatus on the plate of the air-pump, and exhausting the air.

The same methods may be applied to determine the amount of chemically combined water which exists in many compounds, the water of crystallisation of salts, for example. Many bodies, however, retain their water with too great force to be overcome by the means just mentioned. Such substances may be dehydrated by enclosing them in a test-tube immersed in a water or oil-bath, while a current of dry air is drawn through the tube by means of an aspirator. In some cases even this is not sufficient, and the desiccation can only be effected by heating the substance in a tube from which the air is exhausted by an air-pump, then introducing dry air, exhausting again, and so on, till the substance ceases to lose weight. (See Evaporation and Water.)

It is often, however, difficult to determine how much of the oxygen and hydrogen existing in a compound exists in the form of water: for many substances, before they give off all the water that can be eliminated by the methods above described, begin to decompose and form new compounds. In such cases, the process of organic analysis must be applied to the compound in the hydrated state, and the quantity of water estimated as nearly as possible by the phenomena which the substance exhibits when heated, or by its chemical reactions.

Volatile liquids are dehydrated by leaving them for some time in contact with lumps of fused chloride of calcium and then distilling, the chloride of calcium being however previously removed, as it might, when heated, give up some of the water which it has absorbed.

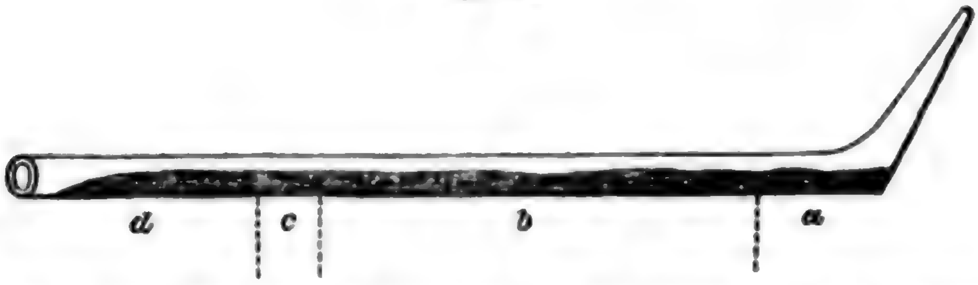
The substance having been brought to the proper state of purity and dryness, may now be subjected to the combustion process.

ESTIMATION OF CARBON AND HYDROGEN.

In Solids not containing Nitrogen.—The substance being thoroughly dry and in the state of fine powder, about 0·3 grm. (or 5 grains) is weighed out in a small test-tube, or between two watch-glasses, the weighing being made exact to the tenth of a milligramme (or ·001 of a grain). The vessel and its contents are weighed together, and after the substance has been removed, the vessel, with the small quantity of matter adhering to it is again weighed. This weight deducted from the former gives the quantity of substance used in the experiment. The combustion-tube after being cleansed, if necessary, is made very hot in the sand-bath, and a long glass tube being thrust into it, the air is sucked out so as to remove every trace of moisture.

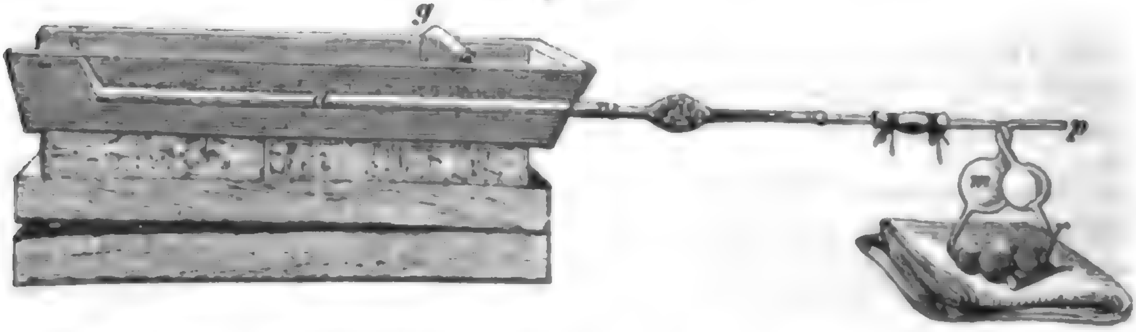
The combustion may be made either with oxide of copper or with chromate of lead; the latter being the more easily managed, on account of its possessing little or no hygroscopic tendencies, we shall describe its use in the first place:—A quantity of the chromate (previously fused and pulverised) sufficient to fill the tube, is heated over a gas lamp till its colour changes to brown-red. When it has cooled, a small quantity is poured into the tube, sufficient to fill about an inch of its length, and about two-thirds of the remainder is poured into a clean dry porcelain mortar. The substance to be analysed is then added to it, and the two are carefully mixed by gentle trituration. The combustion-tube being then taken in the right hand, and the mortar in the left, the mixture is transferred to the tube by a kind of screwing motion, the open end of the tube being slightly inclined upwards after each addition, and the tube lightly tapped against the side of the mortar to make the mixture descend. When nearly the whole of the mixture has been thus introduced, a small quantity of fresh chromate is poured into the mortar, triturated so as to rinse it, and then transferred to the tube in the same manner. The remainder of the tube up to within an inch of the end is filled with pure chromate. The contents of the tube are then shaken together by a few gentle taps on the table, so as to leave a free passage throughout for the evolved gas. The arrangement of the mixture in the tube is shown in *fig.* 20, where *a* represents the pure chromate, *b* the mixture, *c* the rinsings, and *d* the pure chromate near the open end.

Fig. 20.



The tube is now laid in the combustion furnace, and the chloride-of-calcium tube and potash-bulbs are attached to it in the manner already described, the potash-bulbs resting on a folded cloth, and the outer bulb being slightly raised by placing a cork under the apparatus at *r*. *Fig.* 21, represents the arrangement for burning with charcoal. The disposition of the gas-furnace is shown in *fig.* 16, page 225.

Fig. 21.



Before commencing the combustion, the apparatus must be carefully examined to ensure its tightness. For this purpose, a hot coal is held for a short time near the inner bulb (*m*) of the potash apparatus, so as to rarefy the air and cause a few bubbles to pass through the liquid. The coal is then withdrawn, and the apparatus left to itself for about ten minutes. If all the joints are air-tight, the liquid will now rise in the bulb *m* to a higher level than in the outer bulb, and will retain its position; but if any leak occurs, it will soon fall down to its original level. Should this be the case, the leakage is most probably in the cork which fits into the combustion-tube, or in the caoutchouc connector. To remedy this inconvenience without delay, it is well to be provided with two or three well dried perforated corks and a good stock of caoutchouc connectors.

The tightness of the apparatus having been established, the heat may now be applied. The anterior portion of the tube containing the pure chromate is first heated to redness, by laying red-hot charcoal round it (or turning on the gas jets immediately under it). The charcoal furnace is provided with a moveable screen *g*, (*fig.* 21), to prevent the heat from extending too quickly along the tube. When the anterior portion is thoroughly red-hot, the pure chromate of lead at the closed end of the tube must also be heated to redness, in order to burn any vapour that may diffuse into that part of the tube, and to prevent its deposition on the drawn out point, whence it would afterwards be difficult to remove (this precaution must be taken in every combustion, by whatever process). The fire is slowly extended towards the further extremity, each portion of the mixture being thoroughly burnt before the fire is extended further. The combustion should be so regulated that the carbonic acid may enter the potash-bulbs at a uniform rate, and in a succession of bubbles which may be easily counted. If no nitrogen is present, these bubbles are, after a certain time, completely absorbed by the potash; but when an azotised body is burnt, bubbles of nitrogen pass through the potash-solution during the whole process.

When the tube has been heated to redness throughout, the heat must be raised by fanning the fire on the top, and admitting air below by slightly raising the furnace from the bricks. As soon as the evolution of gas begins to slacken, the cork is removed from under the potash-bulbs, and the apparatus brought into the horizontal position. If the combustion has gone on well, the evolution of carbonic acid ceases all at once; if, on the contrary, the gas bubbles continue to pass slowly at intervals for a long time after the tube has been thoroughly ignited, we may be sure that the combustion is imperfect, most probably in consequence of the mixture not having been sufficiently intimate, and that the quantity of carbon will be found deficient.

As soon as the evolution of gas ceases, the liquid begins to rise in the bulb *m*. The coals must then be quickly removed from the end of the tube, and the point broken off with a pair of nippers. If the passage through the tube is clear, the potash-solution immediately falls to the same level in both bulbs: if it does not, there is a stoppage in the tube, and no time must be lost in clearing it, by thrusting in a stout iron wire from end to end; otherwise the potash-solution will be sucked up into the chloride of calcium tube, and the result will be entirely destroyed. To complete the experiment, it is now only necessary to draw a stream of air through the apparatus, by applying the suction-tube (*fig.* 13) to the extremity *p*, of the potash apparatus, so as to draw the small portions of carbonic acid and aqueous vapour remaining in the tube into the chloride of calcium tube and potash-bulbs. In doing this, however, a certain precaution is necessary: for the broken end of the tube being surrounded with an atmosphere of carbonic acid, a portion of this gas is likely to be drawn through the tube into the potash-solution, thereby making the proportion of carbon appear too great. To prevent this, a long glass tube open at both ends is placed over the end of

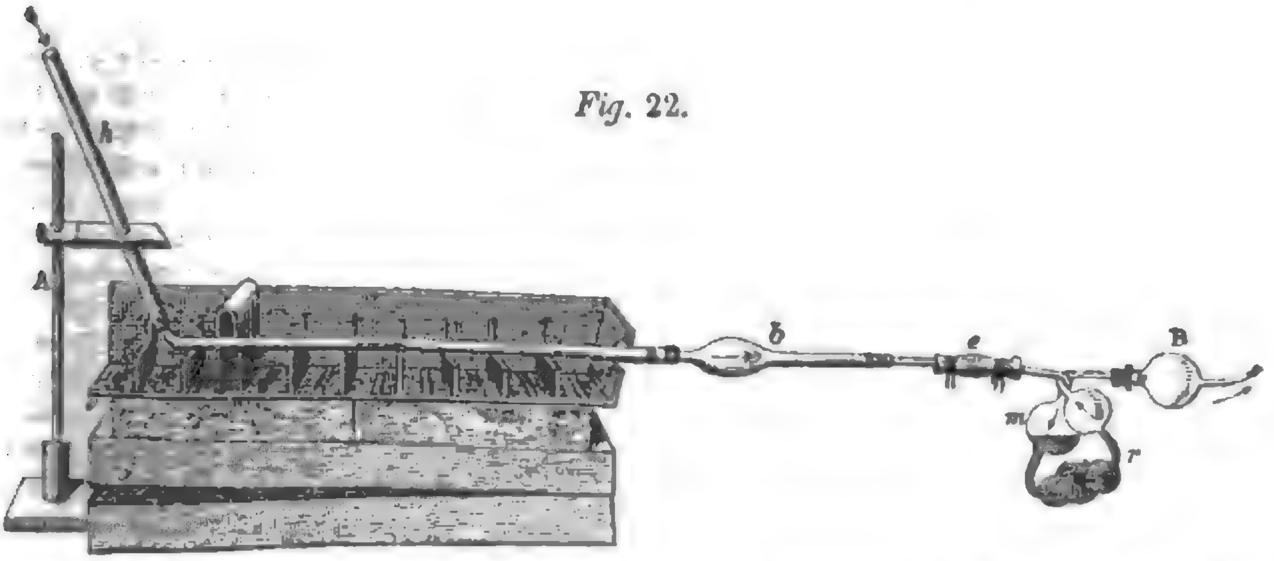


Fig. 22.

the combustion-tube, and supported in a slanting position, as in *fig.* 22, while the air is being drawn through the apparatus. By this means, the air is drawn from a height above the stratum of carbonic acid over the furnace. When the gas furnace is used, this precaution is of course superfluous, as the flame can be extinguished at once.

Lastly, the chloride-of-calcium tube and the potash-bulbs are detached, left to cool for about half an hour, and then weighed. The increase of weight of the potash-bulbs gives the quantity of carbonic acid produced, and $\frac{3}{11}$ of this is the quantity of carbon in the substance analysed. The increase of weight of the chloride-of-calcium tube gives the quantity of water produced, and $\frac{1}{9}$ of this is the amount of hydrogen. Knowing then the quantities of carbon and hydrogen in a given quantity of the substance analysed, it is easy to calculate the proportions of carbon and hydrogen in 100 parts. If the quantities thus determined make up 100, the substance is a hydrocarbon; if there is a deficiency, and it is known that no nitrogen, sulphur, chlorine &c. is present, the difference gives the percentage of oxygen. Examples of the calculation will be given further on.

Combustion with Oxide of Copper. — When the combustion is made with oxide of copper instead of chromate of lead, particular precautions are required to prevent the absorption of water during the mixing and filling of the tube. A quantity of the oxide is heated to redness in a covered earthen crucible, and left to cool till it will no longer burn a cloth in which the crucible is held. It is then mixed in a hot mortar with the substance to be analysed, and the mixture is arranged in the tube between two columns of pure oxide of copper, exactly as described for chromate of lead, the whole operation being conducted as quickly as possible. Some substances, however, will not bear mixing with hot oxide of copper; and even when this can be done, the oxide is sure to cool during the mixing sufficiently to cause an absorption of moisture from the air: hence an excess of hydrogen in the result of the analysis. To obviate this source of error, it is sometimes recommended to lay the tube, after filling, in a trough of hot sand, and connect it with an air-pump, then introduce air dried by passing over chloride of calcium, exhaust again, and so on. This, however, is a troublesome complication of the process. A simpler method of preventing the absorption of water, is to pour the oxide of copper, while still hot, into a long-necked flask (*fig.* 23), closed by a perforated cork in which a chloride-of-calcium tube is inserted, leave it to cool, and mix it with the organic substance in the combustion-tube itself. The neck of the flask must be a little wider than the combustion-tube, so that the latter will just pass into it (*fig.* 24): the oxide may then be transferred to the tube without coming in contact with the air. A small quantity of the cooled oxide is first introduced in this manner, then a portion of the organic substance is added, and upon this a column of oxide about three inches long is poured in the same manner as before. This portion of oxide is mixed with the organic substance by stirring it with a clean iron rod (*fig.* 25), the extremity of which is bent into two turns of a screw; and when it is thoroughly incorporated, the rest of the substance is introduced, then another column of oxide of the same length as before, and the stirring is repeated. Lastly, the rest of the tube is filled with pure oxide, and the combustion performed as above. This method of incorporation does not ensure so complete a mixture of the substance with the oxide as trituration in a mortar; but it answers this purpose sufficiently well in most cases.

Fig. 23.

Fig. 24.

Fig. 25.

Oxide of copper is in many respects more convenient for use than chromate of lead, and indeed is more generally used for the combustion of substances which burn with facility. It is more easily prepared, and when partially reduced by the combustion process, may be restored to its original state by moistening it with nitric acid, and heating it to low redness in a crucible. It then becomes denser and less hygroscopic, and in every way better adapted for use: in fact, it improves in this respect by each repetition of the treatment. Chromate of lead may also be reoxidised by digestion with nitric acid and subsequent fusion; but the pulverisation of the fused mass is a very laborious operation.

On the other hand, there are many cases in which the use of chromate of lead presents decided advantages, viz. in the combustion of substances which are very rich in carbon or difficult to burn, such as fatty bodies, coal, graphite, indigo, &c. Such bodies are never completely burned by oxide of copper, probably because, at the beginning of the combustion, they give off combustible gases, which partially reduce the copper in the neighbourhood of each particle, and leave behind a quantity of charcoal no longer in contact with the oxide, and requiring an atmosphere of free oxygen to burn it. Now chromate of lead fuses when the heat becomes strong, thus becoming more intimately mixed with the combustible substance, and moreover gives off a quantity of free oxygen, which effectually completes the combustion of the carbon. Its efficiency may be still further increased by mixing it with about $\frac{1}{10}$ of its weight of acid chromate of potassium.

Organic salts (tartrates, acetates, &c.) of potassium, sodium, barium, strontium, or calcium, if burnt with oxide of copper, also exhibit a considerable deficiency of carbon, because the metal then remains in the form of a carbonate. This source of error may be obviated by adding to the oxide of copper a quantity of phosphate of copper or oxide of antimony sufficient to decompose the carbonate; or, better, by making the combustion with chromate of lead.

Combustion with Oxide of Copper in a stream of Oxygen. — The oxygen may either be evolved from chlorate of potassium placed in the combustion-tube, or in a vessel connected with it; or it may be previously prepared and supplied from a gas-holder connected with the tube.

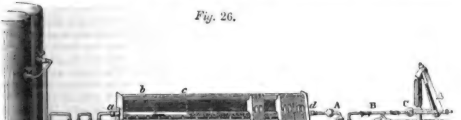
The simplest way of proceeding is to place at the closed end of the combustion-tube about $1\frac{1}{2}$ inch of a mixture of 1 pt. of chlorate of potassium (or better of perchlorate) and 8 pts. oxide of copper, previously heated over a lamp and introduced while hot; then half an inch of pure oxide of copper, then the mixture, and a column of pure oxide as usual. The combustion is carried on in the ordinary manner, until the tube is ignited as far as the pure oxide near the sealed end. Heat is then cautiously applied to the mixture of oxide and chlorate, so as to evolve oxygen at a moderate rate. The carbon is thereby completely burned, and if the supply of oxygen is sufficient, the reduced copper is reoxidised. After the gas has passed through the potash-solution for a few minutes without being perceptibly absorbed, the bulbs and the chloride-of-calcium tube may be detached, without breaking off the point of the combustion-tube, and air drawn through them to displace the free oxygen, which would otherwise increase their weight.

The stream of warm oxygen passing through the potash-solution is sure to carry away a certain quantity of vapour of water. To prevent this, a small tube containing lumps of fused potash should be attached to the bulb apparatus. The apparatus with this addition usually weighs between 50 and 60 grammes.

In operating in the manner above described, there is, however, considerable danger of the stream of oxygen becoming too rapid, and thereby carrying off the vapour faster than it can be absorbed by the solid potash.

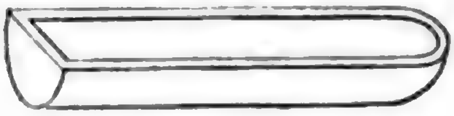
It is better, therefore, to supply the oxygen from a gas-holder. The combustion-tube is open at both ends, and the end *a*, furthest from the potash-bulbs and chloride-of-calcium tube is connected with two gas-holders (*fig.* 26), one filled with atmospheric

Fig. 26.



air, and the other with oxygen gas. The communication is made by means of a T-tube provided with a cock, which renders it easy to connect either gas-holder with the combustion-tube and shut off the other at the same time. The air and oxygen before entering the combustion-tube, are made to pass through two U-tubes, one containing pumice-stone soaked in sulphuric acid, to dry the gas, the other lumps of caustic potash, to free it from carbonic acid. The combustion-tube may be heated either with gas or with charcoal (the figure represents a Babo's gas apparatus), and the mixture may be disposed in the tube in the ordinary way. But instead of mixing the substance with the oxide of copper, it is better in many cases to place it by itself in a small boat of platinum or porcelain *b* (*fig.* 27).

Fig. 27.



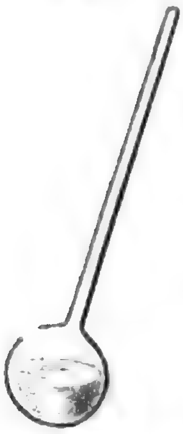
The combustion-tube is first filled to two-thirds of its length with oxide of copper, which need not be previously ignited, the remaining third, nearest to the gas-holder being left free to receive the boat. It is then laid in the furnace, and connected, in the manner just described, with the gas-holder containing atmospheric air; the oxide of copper is heated to redness; and a stream of dry air is passed through the tube so as to remove every trace of moisture. The tube is then left to cool; the boat containing the substance is put into its place, a plug of recently ignited asbestos having been previously introduced to prevent the oxide of copper from coming in contact with it; the chloride-of-calcium tube (U-shaped, see p. 228) and potash-bulbs are attached in the usual manner, and the apparatus is connected with the gas-holder containing oxygen. The oxide of copper is now once more heated to redness, and as soon as it is thoroughly ignited, heat is very cautiously applied to the part of the tube containing the boat, a slow stream of oxygen being passed through the apparatus, sufficient to prevent any backward passage of the evolved gases, but not to cause any free oxygen to pass through the solution of potash. If the oxide of copper exhibits a red colour, arising from reduction, the heating of the substance in the boat must be discontinued till the copper is reoxidised. When at length there is nothing left of the substance but black charcoal, the heat may be increased and the stream of oxygen accelerated. In this manner the combustion is soon completed; and when the bubbles of gas appear to pass through the potash without absorption, the process is continued in the same manner for a few minutes longer, and the potash-bulbs and chloride-of-calcium tube are then detached, after air has been passed through the apparatus for a little while to expel the oxygen. Lastly, the stream of air is continued for a sufficient time to effect the complete reoxidation of the copper, which is then ready for another experiment without further preparation.

After the tube has cooled, the boat is taken out and reweighed. If any inorganic matter remains in it, the quantity of this is at once ascertained if the weight of the boat itself is previously known.

This method, when carefully conducted, gives very exact results: it ensures the complete combustion of the carbon, and obviates all danger of an excess of hydrogen arising from moisture in the oxide of copper. It likewise saves the trouble of igniting the oxide of copper before the experiment, and afterwards treating it with nitric acid, But to ensure a good result, especial care must be taken not to heat the substance in the boat too suddenly; otherwise combustible gases will be given off more quickly than they can be burnt, and the analysis will be worthless.

Combustion of Liquids.—Volatile liquids are enclosed in small glass bulbs with narrow necks (*fig.* 28). The bulb is first weighed and then filled with the liquid, in the same manner as a thermometer tube, viz. by gently warming the bulb so as to rarefy the air, and dipping the neck into the liquid, so that as the air cools, a small quantity of the liquid may be forced up by external pressure. The bulb is then again heated till the liquid boils, the end of the neck immediately plunged again into the liquid, and the heat removed. The vapour now condenses and leaves a vacuum, into which the liquid is forced up so as to fill the bulb and the greater part of the neck. The neck is then sealed, and the bulb re-weighed. It is best to use two bulbs, each containing about 400 milligrammes of liquid.

Fig. 28.



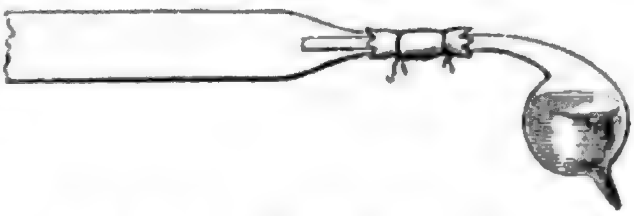
The analysis is made with oxide of copper: the coarse-grained variety obtained by oxidising copper turnings in a muffle, or by breaking oxide which has been hardened by strong ignition into small lumps, and sifting off the finer particles, is best adapted for the purpose, because it affords free space for the passage of the vapours, whereas the fine-grained oxide lies more compactly, and the greater part of the vapour passes over the surface instead of finding its way between the particles. For the same reason, chromate of lead, which fuses into a mass, is not so well adapted for the combustion of volatile liquids. The oxide of copper must be ignited in a crucible and left to cool completely in a corked flask (p. 234).

The combustion-tube should be at least 20 inches long, very volatile liquids requiring even a greater length. About an inch of the cold oxide is first poured in through a wide-necked funnel; one of the bulbs is then taken by the neck, a slight scratch having been previously made on it with a file; it is thrust into the tube, bulb downwards, the neck broken off at the scratch, and both bulb and neck dropt into the tube. About three inches more oxide is then added, the other bulb introduced in the same manner, and the tube filled up with oxide of copper. This oxide is first heated to redness, care being taken to proceed very gradually, and when the charcoal furnace is used, to protect the bulbs by a screen. As soon as the oxide is well ignited, a hot coal is approached to the nearest bulb, so as to volatilise a portion of the liquid, especial care being taken not to drive it over too fast. When the first bulb is empty, the heat is gradually extended; the liquid in the second bulb is then distilled in the same manner, and the combustion is finished in the ordinary way. As soon as the distillation of the liquid commences, a few pieces of hot charcoal must be placed under the point of the combustion-tube, to prevent the liquid from condensing there, as if this occurs, considerable heat will be required to dislodge the liquid, and a sudden burst of vapour is likely to take place.

The object of using two bulbs is to prevent too great a reduction of copper in the neighbourhood of either of them; when there is no longer any oxide close to the bulbs, a deposition of carbon is apt to take place, and then a stream of air or oxygen is required to burn it. Greville Williams, however, uses only one bulb, and drives all the liquid, at the very commencement of the analysis, into a column of cold oxide of copper about four inches long. This portion is not directly heated till the end of the analysis, the liquid being volatilised by the heat conducted by the oxide. Finally, a stream of oxygen is passed through the tube to burn the deposited charcoal. Volatile liquids cannot be burned in a continuous stream of oxygen, because an explosive mixture would be formed.

For extremely volatile liquids, like aldehyde, a different plan is adopted. Such liquids are enclosed in a bulb having the form of a small retort, the neck of which, previously sealed, is inserted into the hinder extremity of the combustion-tube, which is drawn out and left open for the purpose, the connection being made air-tight by means of a caoutchouc tube. As soon as the oxide of copper is ignited, the sealed end of the retort is broken off by pressing it against the combustion-tube, and the liquid is volatilised by cautiously applying the heat of the hand or of tepid water to the bulb. If the liquid is so volatile as to boil at the temperature of the room, the bulb must be immersed in ice, and the evaporation regulated by removing the ice from time to time, and replacing it as soon as the liquid begins to boil.

Fig. 29.



Fixed oils are weighed in a short test-tube, which is then dropped into the combustion-tube,—a small quantity of oxide of copper having been first introduced,—and by inclining the tube, the oil is made to spread itself over the sides for about half the length, after which the tube is filled up with oxide of copper or chromate of lead. Soft, easily fusible fats are treated in the same manner. Waxy bodies are weighed in small lumps, then dropped into the combustion-tube, and spread over its surface by fusion. Fatty and waxy bodies may also be placed in boats in the manner already described (p. 236), and burnt with chromate of lead, or with oxide of copper in a stream of oxygen.

Modification of the Combustion-process in particular Cases:

a. In bodies containing Nitrogen.—When an azotised organic body is burnt, the greater part of the nitrogen is given off in the free state, together with the water and carbonic acid; but a certain portion, varying according to the nature of the substance and the manner in which the combustion takes place, is converted into nitric oxide, or one of the higher oxides of nitrogen. Now, if either of these compounds is formed in the process of organic analysis, it will pass over with the carbonic acid, and if not decomposed before it reaches the potash-ley, it will be absorbed by that liquid and give rise to an error in the estimation of the carbon. Before, therefore, an organic compound is subjected to the combustion process, it must be carefully examined for nitrogen in the manner already described (p. 226), and if that element is found to be present, the combustion must be made in such a manner as to ensure that the whole of it shall be evolved in the free state.

For this purpose a long combustion-tube is taken, and after the mixture and the pure oxide of copper have been introduced in the ordinary way, about five inches of copper-turnings, prepared as described at p. 227, are placed at the open extremity. This metallic copper must be heated in a sand or air-bath just before it is wanted and introduced into the tube while still hot, as its surface is very hygroscopic. The combustion is made in the ordinary way, the metallic copper being however first heated to redness, and kept in a state of strong ignition during the whole process. The nitrogen is then evolved in the free state, and passes through the potash-ley in bubbles.

The combustion must be made with oxide of copper alone: if chromate of lead is used, or a continuous stream of oxygen passed through the tube, the quantity of nitric oxide formed is too large to be effectually decomposed, even by a very long column of red-hot copper. Oxygen may, however, be passed through the tube at the end of the combustion, being evolved for that purpose from chlorate of potassium (p. 235). The more slowly the combustion is conducted, the smaller will be the quantity of nitric oxide formed.

β. *In bodies containing Sulphur.*—When organic bodies containing sulphur are burned with oxide of copper, the sulphur is converted into sulphurous acid, which, if not intercepted, will pass into the potash-solution together with the carbonic acid. This may be prevented, by interposing between the chloride-of-calcium and potash-apparatus, a tube containing peroxide of lead: the sulphur will then be retained in the form of sulphate of lead. It is better however to make the combustion with chromate of lead, placing in the front part of the tube a rather long column of pure chromate, which is heated only to dull redness: the sulphur will then be retained in the combustion-tube.

γ. *In bodies containing Chlorine.*—When chlorinated organic compounds are burnt with oxide of copper, chloride of copper is formed, which being volatile, passes over into the chloride of calcium tube, and renders the determination of the hydrogen inexact. This source of error may be completely avoided by burning with chromate of lead, the chlorine then forming chloride of lead, which is not volatile even at a red heat.

Similarly with bodies containing *bromine* and *iodine.*

δ. *In bodies containing Inorganic Matter.*—If an organic body, when burnt in the air, leaves a residue which gives off carbonic acid on being treated with acids, its analysis by combustion with oxide of copper will not give exact results, because a part of the carbonic acid will be retained in the ash, instead of passing into the potash-bulbs. This is particularly the case with the organic salts of potassium, sodium, barium, strontium, and calcium. If the residue were in all cases a neutral carbonate, its quantity might be determined and the amount of carbonic acid contained in it added to that which is absorbed in the potash apparatus. But this is not the case, the composition of the residue being variable, and depending on a variety of circumstances.

In such cases, the complete evolution of carbonic acid may be ensured in two ways: either by burning with oxide of copper, and mixing the organic substances with ignited phosphate of copper, boric anhydride, or oxide of antimony; or better, by burning with chromate of lead, the alkaline carbonate being then completely decomposed by the chromic acid.—When these organic salts are burnt in a platinum boat, in a stream of oxygen (p. 231), the residue may be weighed, the quantity of carbonic acid in it determined in the ordinary way, and added to that absorbed by the potash.

Amount of Error in the Estimation of Carbon and Hydrogen.—By the methods above described, the carbon may be determined within 0·2 per cent. The error is generally in defect, in consequence of imperfect combustion; sometimes, however, it is in excess, especially in azotised bodies.

The hydrogen may be determined yet more nearly, viz. within 0·1 per cent. The error is usually in excess, arising from absorption of water from the air during the mixing of the substance with oxide of copper. But if this be avoided, by making the mixture in the tube itself, or if the combustion be made with chromate of lead, only a very slight excess of hydrogen need be apprehended. When the substance is burnt in the platinum boat (p. 231), the hydrogen sometimes comes out a little below the theoretical quantity.

ESTIMATION OF OXYGEN.

Oxygen is usually estimated by difference, after all the other elements of the compound have been determined directly. In compounds containing only carbon, hydrogen, and oxygen, this method is sufficiently accurate: for, the error of the carbon being generally in defect, and that of the hydrogen in excess, the two nearly compensate each other; but when chlorine, sulphur, and other elements are present, the errors upon all these being usually in the same direction, viz. in defect, the amount of oxygen determined by difference is likely to be much too great. A good method of determining oxygen directly is therefore a desideratum, more especially as it would afford a check on the estimation of the other elements.

A method of effecting this determination has been given by **Baumhauer** (Ann. Ch. Pharm. xc. 228), and applied in one or two cases. A combustion-tube open at both ends is fitted up in the ordinary way for the determination of carbon and hydrogen, and the two ends of the apparatus are placed in connection with graduated glass tubes, the one at the hinder extremity of the combustion-tube being filled with oxygen, so that, when the combustion is finished, a stream of oxygen may be passed through the tube and re-oxidise the reduced copper. The apparatus is then left to cool, the quantity of gas in the two tubes is read off, and compared with the quantity before the experiment, due regard being paid to corrections for temperature and pressure. The difference gives the quantity of oxygen taken up by the reduced copper. Now, the quantities of carbonic acid and water produced by the combustion having been determined, *the amount of oxygen in this carbonic acid and water, diminished by the quantity of oxygen which has disappeared, gives the quantity of oxygen contained in the substance analysed:* thus, if the amount of oxygen in the carbonic acid and water were 10, and the quantity of oxygen absorbed by the copper were 7, the amount of oxygen contained in the substance would be 3.

Baumhauer gives two analyses (of oxalic acid and oxalate of lead), in which the oxygen was determined by this method with great exactness. As, however, the total volume of gas in the apparatus (the combustion-tube, potash-bulbs, &c.) is not known, but only the difference of volume before and after the experiment, the corrections for pressure and temperature cannot be made with accuracy. For exact results, it is therefore necessary that the pressure and temperature at the beginning and end of the experiment should be nearly the same.

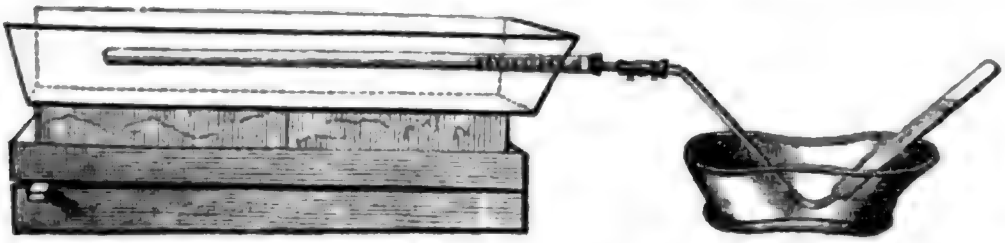
ESTIMATION OF NITROGEN.

The quantity of nitrogen in an organic compound is determined, either by burning the compound with oxide of copper and metallic copper in the manner already described, and measuring the quantity of nitrogen evolved,—or by igniting the compound with soda-lime, whereby the nitrogen is evolved in the form of ammonia, absorbing the ammonia by hydrochloric acid and precipitating by dichloride of platinum.

When the nitrogen is evolved in the free state, it may be estimated in two ways, viz. *comparatively*, that is, by comparison with the quantity of carbon in the compound, previously determined; or *absolutely*, that is, by direct measurement of the whole quantity evolved.

Liebig's Comparative method.—A mixture of the substance (which need not be weighed), with the usual proportion of oxide of copper, is introduced into a combustion-tube of such a length as to be half filled by it, the remainder of the tube being filled up, half with oxide of copper, half with copper turnings. To the mouth of the combustion-tube is fitted a gas-delivery tube, which passes into a trough of mercury and is made flexible by the insertion of a tube of caoutchouc.

Fig. 30.



A screen being placed between the mixture and the pure oxide of copper, the oxide and the metallic copper are first raised to a strong red heat; a second screen is then placed at the back part of the tube, about an inch from the sealed end, and the portion of mixture at that end is ignited, so that the products of the combustion may drive the atmospheric air out of the tube. The combustion of the rest of the mixture is then carried on in the ordinary way, the heat being gradually extended towards the hinder part of the tube, and the mixture of carbonic acid and nitrogen evolved is collected in a number of graduated jars, half an inch in diameter, and twelve or thirteen inches long. These jars must be accurately divided into equal parts of the same value in all; but the absolute value of the divisions may be any whatever.

As soon as one of the tubes is about three-fourths filled with gas, it should be lifted up and the rest of the mercury allowed to run out, so that its place may be supplied with atmospheric air. The object of this is to ascertain whether the gas is free from nitric oxide; if only $\frac{1}{1000}$ pt. of that gas is present, reddish fumes of peroxide of nitrogen will be produced, and if not seen immediately, will become visible on looking along the axis of the tube. If any red or yellow colour is perceptible, another jar must be examined in the same manner, and so on till perfectly colourless gas is obtained. When about six jars have been filled with the gaseous mixture, the process may be stopped, nothing being gained by carrying it to the end.

Fig. 31.

The jars filled with gas are now to be transferred one by one to a tall jar (*fig.* 31), containing mercury, and the proportion of carbonic acid and nitrogen in each of them determined, by first bringing the mercury to the same level inside and out, and reading off the volume of the gaseous mixture, then absorbing the carbonic acid by a strong solution of caustic potash, introduced by means of the curved pipette A, and reading off the volume of nitrogen left. If the combustion has been properly conducted, the proportion of carbonic acid and nitrogen should be the same in all the jars.

Now, a molecule of anhydrous carbonic acid CO^2, containing 1 atom of carbon [= 12], occupies the same volume as a molecule (or double atom) of nitrogen, NN [2 . 14 = 28]. If therefore, the volumes of carbonic acid and nitrogen in the gaseous mixture are to one another as $m : 1$, it follows that the number of carbon-atoms is to the number of nitrogen-atoms as $m : 2$, and consequently the weight of the carbon in the compound is to that of the nitrogen as $m \times 12 : 2 \times 14$, or as $3m : 7$; so that, if the percentage of carbon (c) be previously found, the percentage of nitrogen (n) will be given by the equation:

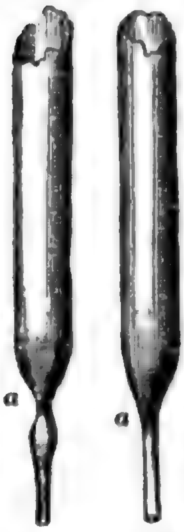
$$n = \frac{7}{3m} c.$$

For example, caffeine, which contains 49·48 per cent. of carbon, is found by the process just described to yield carbonic acid and nitrogen in the proportion by volume of 4 : 1; the percentage of nitrogen in caffeine is therefore $\frac{7}{3 \times 4} . 49·48 = 28·89$.

This comparative method of estimation yields perfectly satisfactory results for all compounds in which the proportion of nitrogen to carbon is not less than 1 : 8, provided the combustion is conducted in such a manner as to avoid the evolution of nitric oxide. The risk of error from this source is less, *the more intimately the organic substance is mixed with the oxide of copper, and the more slowly the combustion is performed.* This rule applies to all combustions of azotised bodies.

Liebig's comparative method has been variously modified by different chemists. Bunsen has contrived a form of apparatus by which it may be carried out with accuracy, even when the proportion of nitrogen is very small, and with not more than a few centigrammes of substance. This method consists in burning the substance with oxide of copper and metallic copper in a sealed tube filled with hydrogen, and analysing the resulting mixture of carbonic acid and nitrogen in a carefully graduated eudiometer.

Fig. 32.



A tube of thick Bohemian glass, about 15 inches long, and $\frac{3}{4}$ of an inch internal diameter, is drawn out at one end in the form of a cone, as shown at *a* (*fig.* 32), and the part *a* is then heated in the blowpipe flame till it is contracted and the glass very much thickened. A mixture of 3 to 5 centigrammes of the organic substance, with 5 grms. of oxide of copper, is now introduced into the tube, together with a few copper turnings, and the other end of the tube is drawn out and thickened in the same manner as the first. The tube is then connected at one end with a hydrogen-apparatus, *fig.* 33 (A being the generating vessel, and B a receiver containing sulphuric acid to dry the gas), and at the other with an exhausting syringe. The hydrogen, after passing through the tube, escapes by the cock *p*.

As soon as all the air is expelled, the cock *p* is closed, the cork of the generating vessel loosened, the caoutchouc tube *c* tightly tied, the tube partially exhausted by a stroke of the pump, and the cock *s* immediately closed. The tube is now sealed at *d* and *b* with the blowpipe flame, the sealing being much facilitated by the partial exhaustion. The next step of the process is to heat the tube to redness, having first enclosed it in a mould of gypsum, to prevent it from being blown out by the expansion of the enclosed gases. For this purpose, the two halves of a cylindrical mould of iron plate, shown in *fig.* 34, are filled with gypsum paste mixed with a few cow-hairs, and as soon as the plaster begins to set, the tube is laid in one half of the mould, the other half put on, and the two firmly wedged together. The apparatus is then heated to low redness for an hour, the tube taken out when quite cold, and one of the sealed ends broken off under a graduated jar full of mercury, so that the mixture of carbonic acid and nitrogen in the tube may pass up to the top of the jar. The gaseous mixture is moistened by passing up a drop of water, then accurately measured, with due regard to corrections for pressure and temperature, and afterwards freed from carbonic acid by thrusting up into it a ball of fused potash, fixed at the end of an iron wire (see **Analysis of Gases**), the ball being first moistened by breathing on it. This ball is then withdrawn, and another ball of dry potash introduced for the purpose of drying the gas, after which the residual nitrogen is measured. The proportion of carbon and nitrogen is then calculated in the manner already described.

Fig. 33.

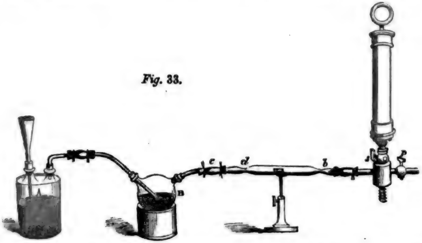
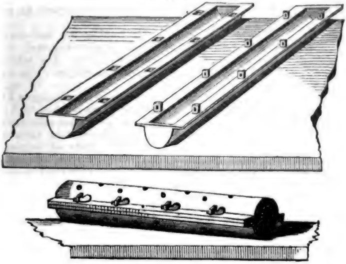


Fig. 34.



Other modifications of Liebig's method have been introduced by Dr. **Maxwell Simpson** (Chem. Soc. Qu. J. vi. 290), by **Marchand** (J. pr. Chem. xl. 177) and by **Gottlieb** (Ann. Ch. Pharm. lxxxviii. 241).

b. Absolute method.—The organic compound is burnt with oxide of copper, as before, and the whole quantity of carbonic acid and nitrogen collected. In the form originally given to this process by Liebig, the carbonic acid and nitrogen were collected in a graduated jar, containing air and standing over mercury, the gas-delivery tube being bent so as to pass up through the mercury into the air in the jar. The volume of air was carefully noted before the experiment, also the volume of air and gas when the combustion was finished and the apparatus had been left to cool, the observed volumes being in each case reduced to the standard pressure and temperature; the increase gave the volume of carbonic acid and nitrogen produced by the combustion. The volume of carbonic acid was then calculated from a previous determination of the carbon, and this, deducted from the volume of the mixed gases, gave the quantity of nitrogen by volume, from which the weight was calculated. For example, 0·1 grm. caffeine burnt in this manner yields 114·06 cub. cent. of gas at 0° C. and 28" bar. The same quantity burnt in the ordinary way yields 0·181 grm. carbonic acid, corresponding to 91·09 cub. cent. at 0° C. and 28 inches of the barometer: consequently 0·1 grm. caffeine yields 114·06 − 91·09 = 22·85 cub. cent. nitrogen gas = 28·86 per cent. by weight.

The process in this form is liable to numerous sources of error. In the first place, the necessary limits to the the size of gas jars standing over mercury, restricts the quantity of substance burnt to 1 or 2 decigrammes; and with this small quantity the errors of observation and manipulation bear too great a proportion to the whole to give even a good approximation to the truth, unless the proportion of nitrogen is rather large. Very considerable errors may arise from the alteration in the dimensions of the tube, likely to result from softening by heat, and from the consumption of a portion of the oxygen of the air in the tube during the combustion. (*For the details of the process*, see *Handwörterbuch d. Chemie*, 2^te^ Aufl. i. 873.)

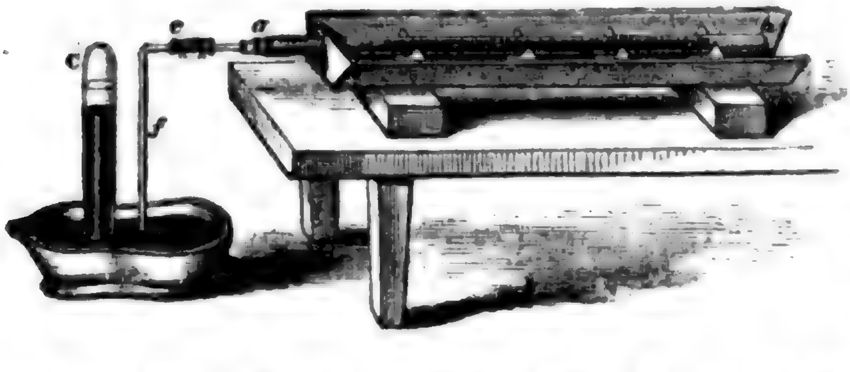
To remove these sources of error, the process has been modified by Dumas and others, so as to make the result independent of the volume of air in the apparatus. This is effected by replacing the air by another gas, which can afterwards be removed by absorption, and sometimes also by exhausting with the air-pump.

In Dumas's process, the air is removed from the combustion-tube, partly by exhaustion with the air-pump, and partly by a stream of carbonic acid gas evolved from carbonate of copper placed at the sealed end of the tube. The combustion is then performed; the carbonic acid and nitrogen evolved by it are collected in a graduated jar standing over mercury, and containing also solution of potash, which absorbs the carbonic acid; and, when the combustion is finished, the carbonate of copper is again heated, so as to evolve carbonic acid, and sweep all the remaining nitrogen into the jar. The volume of nitrogen is then observed, with due regard to pressure and temperature.

This process gives accurate results; but it is troublesome, and requires rather complicated apparatus. A simpler form of it is now generally used, in which the exhaustion with the air-pump is dispensed with by the use of a substance which evolves carbonic acid more abundantly than carbonate of copper. This simplification is due to Melsens. (Ann. Ch. Pharm. lx. 115.)

Fig. 35.

Fig. 36.



At the sealed end of a combustion-tube 30 inches long, is placed a layer, 6 inches long, of acid carbonate of sodium, *a b* (*fig.* 35); then oxide of copper, *b c;* then the mixture of the organic substance with oxide of copper, *c d;* then strongly ignited oxide of copper, *d e;* and, lastly, copper turnings, *e f*. The tube is enveloped in copper foil or brass wire gauze, and connected by a gas delivery-tube with a graduated jar, standing over mercury (*fig.* 36), and partly filled with strong solution of potash. The tube is laid in the combustion furnace, and the acid carbonate of sodium gradually heated, the other part of the tube being protected by a screen. Carbonic acid gas is then evolved, and drives the air out of the tube. It is tested from time to time by collecting it in small tubes filled with mercury, and passing caustic potash into it. As soon as the gas is completely absorbed by the potash-ley, showing that all the air is expelled from the tube, the heat is removed from the acid carbonate of sodium; the graduated jar, filled partly with mercury, and partly with potash-ley, is adjusted in its place over the extremity of the delivery-tube, and the combustion is commenced. The nitrogen and carbonic acid then pass over together; the carbonic acid is absorbed by the potash; and the nitrogen collects in the jar. When the combustion is finished, heat is again applied to the acid carbonate of sodium, so as to evolve more carbonic acid, and sweep all the residual nitrogen into the gas jar.

The gas is left standing over the caustic potash till the absorption of the carbonic acid appears to be quite complete: it may be accelerated by a gentle agitation. A ground glass plate is then placed under the jar, pressed against it, to prevent the mercury from running out, and the jar is transferred from the mercury-trough to a large vessel of water. On removing the glass plate, the mercury and potash-ley run out, their place being supplied by water. The volume of the gas is then read off, and reduced to the standard pressure and temperature, allowance being also made for the tension of the aqueous vapour. From the corrected volume of nitrogen thus obtained, the weight is easily deduced by calculation.

If commercial bicarbonate of soda is used in this process, it must be tested beforehand, in order to ascertain whether it gives off any gas not absorbable by potash. Indeed, it is advisable to subject all the materials used in the process to a trial by ignition without the organic substance. They ought not to yield more than ½ to 1½ c. c. of gas not absorbed by potash-ley.

It is also of the greatest importance, in all nitrogen estimations in which the nitrogen is determined by volume, to test carefully the accuracy of the weights with which the substance to be analysed is weighed out. In other analyses, the absolute value of the weights used is unimportant, provided they agree amongst themselves; but if the gramme weight and its subdivisions, with which the substance is weighed out, are not true to their standard values, the weight of the nitrogen, determined by calculation from its observed volume, according to fixed data, will not give the true weight of nitrogen contained in the compound.

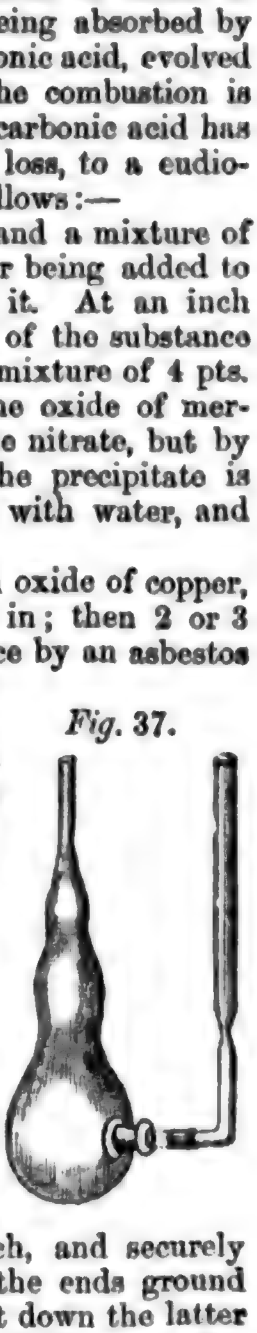
Another modification of Dumas's process is given by Dr. **Maxwell Simpson** (Chem. Soc. Qu. J. vi. 299). The combustion is made with a mixture of oxide of copper and mercuric oxide, the free oxygen evolved by the latter being absorbed by red-hot copper, and the atmospheric air expelled by a stream of carbonic acid, evolved from carbonate of manganese. The gaseous mixture evolved by the combustion is collected in a receiver of peculiar construction, from which, after the carbonic acid has been absorbed by potash, the nitrogen can be transferred, without loss, to a eudiometer, and accurately measured over mercury. The details are as follows:—

A combustion-tube, from 2½ to 3 feet long, is sealed at one end, and a mixture of 12 grm. carbonate of manganese and 2 grm. mercuric oxide (the latter being added to prevent the possible formation of carbonic oxide) is introduced into it. At an inch from this mixture is placed a plug of asbestos, and then the mixture of the substance to be analysed (5 or 6 decigm.) with about 45 times its weight of a mixture of 4 pts. oxide of copper and 5 pts. oxide of mercury. To ensure that the oxide of mercury is free from nitrogen, it must be prepared, not by ignition of the nitrate, but by precipitating corrosive sublimate with excess of caustic potash; the precipitate is washed with aqueous phosphoric acid, to remove free potash, then with water, and dried at a rather strong heat.

The mixture having been introduced, the mortar is rinsed out with oxide of copper, and the rinsings added as usual; then a plug of asbestos is thrust in; then 2 or 3 inches of pure oxide of copper added, this also being kept in its place by an asbestos plug; and the tube is filled up with metallic copper, prepared by reducing the coarse-grained oxide (p. 226) with hydrogen. The open end of the tube is then drawn out, and the neck joined by a caoutchouc connector with a gas delivery-tube, bent at right angles and dipping into the mercury-trough.

The combustion-tube is now laid in the furnace, and heat is applied to the metallic copper and oxide of copper, and at the same time to the carbonate of manganese, the heated portions being shut off by screens from the middle of the tube; and as soon as the air is completely expelled from the tube by the stream of carbonic acid, the mixture of the organic substance with the oxides is heated in the usual way, from the front backwards, the tube being first connected with the vessel intended to receive the nitrogen. This vessel has the form shown in *fig.* 37, and a capacity of about 200 cub. cent.: the external diameter of the upper part should not exceed 7 or 8 mm. A tube of thick vulcanised caoutchouc, 1½ inch long, is slipped over the top, which it must accurately fit, to the extent of half an inch, and securely bound round with silk cord. A glass rod, half an inch long, with the ends ground flat, and having the same diameter as the caoutchouc tube, is thrust down the latter till it touches the gas vessel. A piece of thermometer tubing, also of the same diameter, and having a fine hair-bore, is bent into the form shown in *fig.* 38, and also

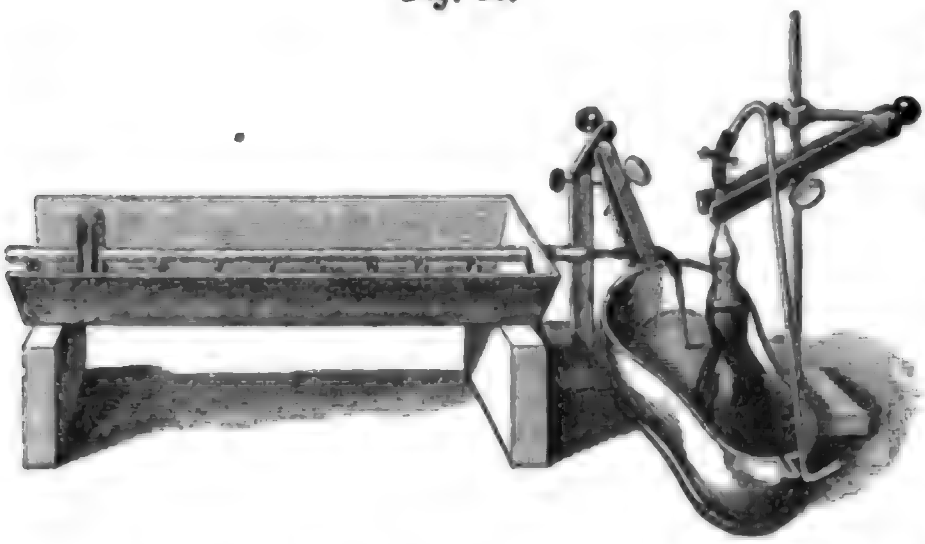
Fig. 37.



inserted. The caoutchouc is next slightly stretched over it, and firmly secured with silk cord, so that there may be no interval between the glass rod, bent tube, and gas vessel. A silk cord is, lastly, tied round the part of the caoutchouc tube where the solid rod lies, so as to make it perfectly air-tight. Before using the apparatus, the joints must be tested by partially filling it with mercury, plunging the mouth beneath the surface of the liquid, and observing if the level remains constant.

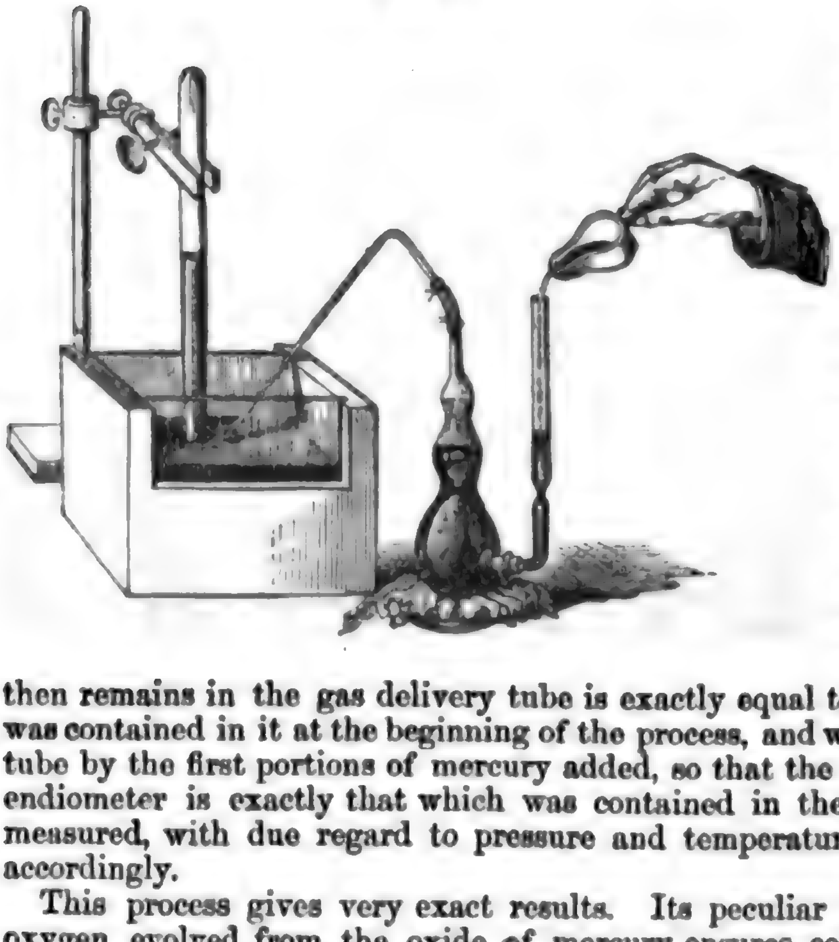
The apparatus is completely filled with mercury and caustic potash solution, and placed in the mercurial trough as shown in *fig*. 38. The gas delivery-tube, proceeding from the combustion-tube, being then inserted into its lateral opening, the products of combustion pass into it, the carbonic acid being absorbed by the potash-ley, while the nitrogen remains. At the termination of the combustion, the nitrogen still remaining in the tube is swept out into the receiver by a stream of carbonic acid, evolved by heating the portion of carbonate of manganese still remaining undecomposed.

Fig. 38.



The next thing to be done is to transfer the nitrogen to a eudiometric tube. For this purpose a bent tube, narrowed towards the lower part of the upright arm is fitted air tight to the lateral opening of the receiver by means of a cork, care being taken that no air is introduced in fitting it, to ensure which it is best to moisten the cork with a solution of corrosive sublimate. Mercury is now poured into the bent tube, and the receiver is lifted out of the mercury, carried to a mercurial trough with glass sides (*fig*. 39), and allowed to stand for an hour or two, so that the absorption of the carbonic acid may be complete. A eudiometer, previously moistened with a drop of water, so that the gas may be saturated with moisture, is then carefully filled with mercury, and inverted in the trough; the end of the gas delivery-tube from the receiver is brought under it; the cord which tied the caoutchouc tube to the glass rod is removed; and the nitrogen is driven into the eudiometer by slowly pouring mercury into the bent tube, as shown in the figure. As soon as the potash-ley makes its appearance in the gas delivery-tube, the addition of mercury is stopped. The volume of nitrogen which then remains in the gas delivery tube is exactly equal to the volume of the air which was contained in it at the beginning of the process, and was driven into the eudiometer tube by the first portions of mercury added, so that the volume of gas driven into the endiometer is exactly that which was contained in the receiver. Lastly, the gas is measured, with due regard to pressure and temperature, and the weight calculated accordingly.

Fig. 39.



This process gives very exact results. Its peculiar advantages are, that the free oxygen evolved from the oxide of mercury ensures complete combustion, while the vapour of mercury prevents the formation of any oxides of nitrogen: moreover, it enables the gas to be measured over mercury, which is much more exact than the ordinary mode of measuring over water.

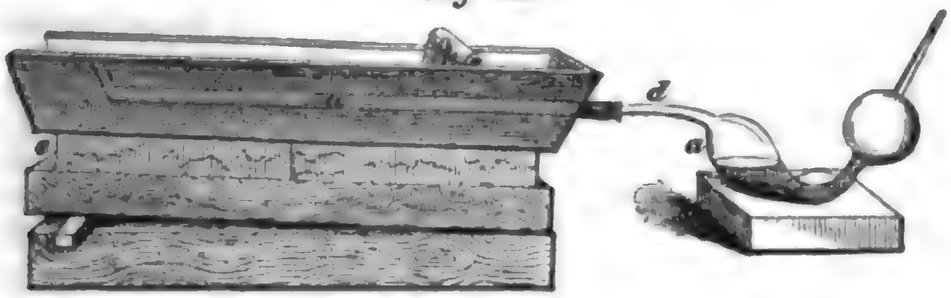
Estimation of Nitrogen by Will and Varrentrapp's Method.—Most azotised organic bodies heated with hydrate of potassium or sodium, give off the whole of their nitrogen in the form of ammonia, the carbon uniting with the oxygen of the alkaline hydrate to form carbonic acid, while the hydrogen combines with the nitrogen to form ammonia. If the quantity of nitrogen present is not sufficient to unite in this manner with all the hydrogen, the remainder is evolved as gas; but there is no organic substance, excepting those containing nitric acid, in which the quantity of nitrogen is too great to be completely converted into ammonia by the hydrogen thus liberated from the alkaline hydrate. In many cases, however, cyanide of potassium or sodium is formed in the first instance; but even then, if a sufficient excess of the alkaline hydrate is present, the cyanogen is decomposed when the heat becomes very strong, and the whole of the nitrogen is given off as ammonia. It is on these facts that Will and Varrentrapp's method of estimating nitrogen is founded.

As the hydrates of potassium and sodium are very deliquescent, and act strongly on glass at high temperatures, it is convenient to mix them with quick lime, which makes them more manageable, and diminishes their action on the glass. The mixture generally used is *soda-lime*, containing 1 pt. of hydrate of sodium, and 2 pts. of quick lime. It is prepared by adding the requisite quantity of quick lime to caustic soda-ley of known strength, evaporating to dryness in an iron pot, calcining the residue in a crucible, and afterwards rubbing it to fine powder in a warm mortar. It must be preserved in wide-mouthed vessels with good stoppers. If commercial soda is used for this purpose, it must be previously tested for nitric acid, as the presence of that compound would vitiate the analysis.

The substance to be analysed is mixed in a warm porcelain mortar, with a quantity of soda-lime sufficient to fill about two-thirds of a combustion-tube, from 16 to 18 inches long. The soda-lime must be previously heated over a lamp to expel any moisture or ammonia that it may have absorbed, and the mixture must be made by very gentle trituration, otherwise portions of it will adhere obstinately to the mortar and pestle. After it has been introduced into the tube, the mortar is rinsed with fresh soda-lime, and finally with pounded glass, to remove any small portions of adhering matter. Lastly, the tube is filled up with soda-lime to within an inch of the extremity, a plug of ignited asbestos being placed at the end to prevent the light powder from being carried forward by the vapours.

The ammonia is collected in a bulb-apparatus of the form shown in *fig.* 40, containing hydrochloric acid (specific gravity about 1·10), sufficient to half fill one of the larger bulbs. This apparatus is adapted to the combustion-tube in the manner shown in the figure, and the tube is gradually heated from end to end. Ammonia is then given off and is absorbed by the hydrochloric acid. Towards the end of the combustion, the heat must be very much increased, in order to decompose any cyanide of sodium that may have formed in the earlier stage of the process. When the combustion is finished, the point of the tube is broken off, and air drawn through the apparatus in the usual way. Bouis (Bullet. Soc. Chim. de Paris, i. 105) recommends to place at the closed end of the tube a mixture of oxalate of calcium and slaked lime (obtained by neutralising oxalic acid with milk of lime, boiling the precipitate with excess of lime, and drying rapidly at 110° C.) which, when decomposed at the end of the operation, evolves a stream of hydrogen that sweeps all the ammonia remaining in the combustion-tube into the acid placed to receive it.

Fig. 40.



The acid liquid is emptied into a capsule, and the bulbs are rinsed with alcohol, and then repeatedly with distilled water. Sometimes oily hydrocarbons are formed during the combustion, and collect on the surface of the acid liquid. In this case it is best, before proceeding further, to separate the oil from the acid liquid by filtration, the filter being previously moistened with water. Bichloride of platinum is now added to the acid solution, which precipitates the ammonia as chloroplatinate of ammonium, $NH^4Cl . PtCl^2$; the whole is evaporated to dryness over the water-bath; and the dry mass when cold, is treated with a mixture of 2 volumes of strong alcohol and 1 vol.

ether, which dissolves the excess of bichloride of platinum, and leaves the chloroplatinate of ammonium. This salt is collected on a weighed filter, washed with the same mixture of alcohol and ether, then dried at 100° and weighed; 100 pts. of it correspond to 6·279 pts. of nitrogen. Or, the salt with its filter may be ignited in a weighed crucible of platinum or porcelain, till the filter is completely burned to ashes and metallic platinum is left. The ignition must be performed with great care, commencing with a very gentle heat, which should be increased very gradually, because the vapours of sal-ammoniac and chlorine which escape are very apt to carry with them a small quantity of platinum: 100 pts. of platinum correspond to 14·204 pts. of nitrogen.

The process just described may be applied to most azotised organic bodies without further modification. Sometimes, however, when the proportion of nitrogen is large, as in urea, mellone, &c., the whole of the hydrogen is given off as ammonia. In this case, the quantity of uncondensable gas evolved is comparatively small, and towards the end of the process, the acid in the bulbs is very likely to be suddenly drawn back into the combustion-tube. This accident may be prevented by adding to the mixture a small quantity of sugar or tartaric acid, so as to dilute the ammonia with uncondensable gases.

Liquids containing nitrogen may be treated in the same manner, being enclosed in bulbs, as for combustion with oxide of copper.

There are some azotised organic bodies to which Will and Varrentrapp's process is not applicable,—those, namely, in which the nitrogen exists in the form of an oxide, generally as NO^2 (the so-called nitro-compounds): these bodies, when ignited with an alkaline hydrate, giving off only a portion of their nitrogen in the form of ammonia, so that the quantity found is always too small.

Other azotised bodies, when heated with soda-lime, give off, not ammonia, but organic bases free from oxygen, and more or less resembling ammonia. Thus indigo yields phenylamine (C^6H^7N), and many non-volatile organic bases, *e.g.* narcotine, morphine, quinine, and cinchonine, give off organic volatile bases. Many non-oxygenised organic bases, such as phenylamine, chinoline, &c., pass over ignited soda-lime without decomposition, or at all events do not yield all their nitrogen in the form of ammonia. Now all these volatile organic bases form platinum-salts, in which, as in chloroplatinate of ammonium, 1 atom of platinum corresponds to 1 atom of nitrogen. If, therefore, these bases are treated by Will and Varrentrapp's process, the resulting platinum-salts ignited, and the metallic platinum weighed, 100 pts. of it will correspond to 14·204 pts. of nitrogen, whatever organic base may have been formed in the decomposition. As, however, the platinum-salts of many of these bases are more soluble in alcohol than chloroplatinate of ammonium, it is best to wash them, not with the mixture of alcohol and ether above-mentioned, but with absolute ether to which only a few drops of alcohol are added. In all cases in which it is not certainly known that the body submitted to analysis gives off the whole of its nitrogen as ammonia, the chloroplatinate should be ignited after being weighed, and the residual platinum weighed again, so as to ascertain whether the chloroplatinate weighed was really chloroplatinate of ammonium. (NH^4PtCl^3 corresponds to 44·3 per cent. platinum.)

Instead of precipitating the ammonia with bichloride of platinum, its quantity may also be determined volumetrically, for instance, by receiving it in dilute sulphuric acid of known strength, and estimating the quantity of free acid remaining by means of a standard alkaline solution. Péligot uses for this purpose dilute sulphuric acid, containing 61·25 grms. of SO^4H^2, in a litre of liquid; neutralises it with a measured quantity of a solution of lime in sugar-water; and compares the quantity of the lime-solution required for this purpose with that which is required to neutralise the same volume of acid after absorption of the ammonia. Instead of the solution of lime in sugar-water, which quickly varies in strength, and must be standardised before each experiment, it is better to use a standard solution of caustic soda (see ACIDIMETRY, and ANALYSIS VOLUMETRIC). If an acid be used containing 1 at. SO^4H^2 in a litre of liquid, and a solution of soda containing 2 at. NaHO in the same volume of liquid, the quantity of acid saturated by the ammonia will be very readily found, and thence also the quantity of ammonia absorbed. These methods, being more rapidly executed than the platinum-determination, are especially applicable in the determination of nitrogen for technical purposes, in the valuation of guano for example.

Other modifications of Will and Varrentrapp's process have been proposed, for example, receiving the ammonia in tartaric acid,—but they do not appear to present any peculiar advantages.

ESTIMATION OF CHLORINE.

Organic bases combine with hydrochloric acid, forming salts (the hydrochlorate of morphine, for example), from the solutions of which chlorine may be completely precipitated by simply adding nitrate of silver. But many organic compounds contain chlorine in a form in which it cannot be precipitated as chloride of silver, until the compound is completely destroyed.

The mode of decomposition adopted in such cases is to ignite the compound with a caustic alkali or alkaline earth, generally with quick lime. The lime used for the purpose is obtained by subjecting marble to a strong red heat in a crucible. It must be tested for chlorine, and if that element is found in it, the lime must be slaked, and the chloride of calcium separated from it by washing with water, after which it is to be recalcined.

The organic compound, if solid, is mixed in a mortar with the pure pounded lime, the mixture introduced into a combustion-tube from 12 to 18 inches long, and the tube filled-up with pure lime, or (in order to diminish the quantity of lime which has to be subsequently dissolved in nitric acid) with a mixture of lime and pounded glass. The mixture is then burnt in the usual manner; afterwards, while the tube is still hot, the open end is closed by a cork, it is then wiped with a piece of filter-paper, and gradually introduced into a tall glass cylinder about one-third full of cold distilled water: the hot tube breaks on thus coming in contact with the water, and its contents fall into the cylinder, where the excess of lime is dissolved by nitric acid. The liquid is then filtered, if necessary, and the chlorine precipitated by nitrate of silver. Or, the contents of the tube when cold are turned out into a jar of distilled water, and the whole is dissolved by nitric acid. This method, however, is more subject to error than the first; for it is difficult to prevent a portion of the very fine dust of lime being carried away by the air while emptying the tube into the water.

Liquids containing chlorine are enclosed in bulbs in the manner already described (p. 232), and the vapours passed over the red-hot lime.

Bromine and *iodine* in organic compounds are estimated in like manner.

ESTIMATION OF SULPHUR.

Sulphur is sometimes contained in organic compounds in such a manner that it exhibits its usual reactions with metallic solutions; more generally, however, its separation can only be effected by the complete destruction of the compound. In some cases, oxidation with strong nitric acid will effect the decomposition, the sulphur being converted into sulphuric acid; but a more certain method is to fuse the compound with an alkaline hydrate or carbonate, mixed with nitre, chlorate of potassium, or oxide of mercury.

For non-volatile bodies, a few lumps of hydrate of potassium are fused in a silver crucible over a gas lamp, with about $\frac{1}{8}$ of nitre, a few drops of water being added to facilitate the fusion; a weighed quantity of the sulphuretted organic compound is then added in successive small portions, and the heat is gradually raised, small quantities of nitre being thrown in from time to time, if necessary, to burn away the carbon. The fused mass when cold is dissolved in boiling water, the excess of alkali neutralised with hydrochloric acid, chloride of barium then added, and the precipitate of sulphate of barium filtered, washed, and ignited with the usual precautions. (See SULPHURIC ACID.)

Sulphur-compounds may also, whether fixed or volatile, be burnt in a combustion-tube with a mixture of carbonate of sodium, with nitre, chlorate of potassium (Kolbe), or oxide of mercury (Russell, Chem. Soc. Qu. J. vii. 212),—non-volatile pulverisable solids being mixed up with the carbonate of sodium and the oxidising agent, volatile liquids being enclosed in sealed bulbs, and volatile solids and fatty bodies placed in platinum boats.

ESTIMATION OF PHOSPHORUS.

Phosphorus in organic bodies is estimated by burning the substance with a mixture of alkaline carbonate and nitre or chlorate of potassium, in the same manner as for sulphur, and precipitating the resulting phosphoric acid as phosphate of magnesium and ammonium. Similarly for *arsenic*.

Other non-volatile substances occurring in organic compounds are estimated by the ordinary processes adapted to each of them, in the residue left after the organic matter has been burnt away.

An easier method of estimating sulphur, phosphorus, chlorine, &c., in organic compounds, lately introduced by Carius (Ann. Ch. Pharm. cxvi. 1), consists in heating the substance with nitric acid, of specific gravity about 1·2, in a sealed tube. *Sulphur* is thereby, in nearly all cases, completely converted into sulphuric acid, and may be precipitated by chloride of barium; *phosphorus* and *arsenic* are converted into phosphoric and arsenic acids, and may be precipitated as ammonio-magnesium salts; *chlorine* is partly oxidised, partly separated in the free state, but may be completely converted into hydrochloric acid by means of a dilute solution of sulphurous acid or sulphite of sodium, and then precipitated by nitrate of silver; *bromine* and *iodine* are completely separated in the free state, and may be estimated in like manner; lastly, *metals* are converted into oxides or nitrates, and may be estimated by the ordinary methods of mineral analysis.

This method of oxidation by nitric acid in sealed tubes, is likewise applicable to many inorganic compounds, the sulphides of arsenic, for example. (For details, see the articles CHLORINE, PHOSPHORUS, SULPHUR, &c.)

DETERMINATION OF THE CHEMICAL FORMULA OF AN ORGANIC COMPOUND.

When the quantities of the several elements of a compound which make up a given weight, say 100 parts, are known, it is easy to calculate the *relative* number of atoms of these elements. For, since the actual weight of a substance (W) is equal to the weight of each atom (A), multiplied by the number (n) of the atoms ($W = n\,A$), it follows that the number of atoms is equal to the total weight divided by the atomic weight ($n = \frac{W}{A}$); so that, when the percentage composition is known, the relative numbers of the atoms—in other words, the empirical formula—will be found by dividing the percentage of each element by its atomic weight, and reducing the result to its simplest numerical expression.

For example, sorbic acid is found by Hofmann's analysis (Chem. Soc. Qu. J. xii. 46) to contain in 100 parts: 64·38 C, 7·20 H, and 28·42 O. Therefore:

$$\text{Number of Carbon-atoms} = \frac{64{\cdot}38}{12} = 5{\cdot}36 \text{ or } 3$$

$$\text{,, Hydrogen-atoms} = \frac{7{\cdot}20}{1} = 7{\cdot}20 \text{ or } 4$$

$$\text{,, Oxygen-atoms} = \frac{28{\cdot}42}{16} = 1{\cdot}77 \text{ or } 1$$

consequently, the simplest atomic expression of the constitution of sorbic acid is C^3H^4O.

Whether this is the real expression for the composition of the molecule, or whether it should be $C^6H^8O^2$, or $C^9H^{12}O^3$, or any other multiple of the first formula, must be determined by other considerations. In the case of an acid, we naturally look to the constitution of its salts, the barium- and silver-salts being generally selected as being the most easily prepared and analysed. The analysis of sorbate of barium gives:

	In 100 pts.		at. wt.		No. of atoms.
Carbon . . .	40·37	÷	12	=	3·36 or 6·08
Hydrogen . . .	4·02	÷	1	=	4·02 or 7·27
Barium . . .	37·89	÷	68·5	=	0·55 or 1
Oxygen . . .	17·72	÷	16	=	1·11 or 2
	100·00				

This approaches very nearly to the formula $C^6H^7BaO^2$, showing that the rational formula of sorbic acid is, not C^3H^4O, but $C^6H^8O^2$, supposing the acid to be monobasic, or $C^{12}H^{16}O^4$, if it is dibasic. Which of these hypotheses is correct must be determined by other considerations (ACIDS, p. 46). The monobasic formula is adopted because it is found that sorbic acid forms but one class of salts, one ether, one amide, &c.

The rational formulæ of bases are also determined by the constitution of their salts. The platinum-salts are most generally relied on, because they can be easily obtained pure, and the platinum can in most cases be determined with great accuracy. The rational formula of the base is that which corresponds to 1 atom of platinum. Thus the platinum-salt of *nitranisidine* gives numbers corresponding to the formula, $C^7H^8N^2O^3.HCl,PtCl^2$: hence the formula of the base is $C^7H^8N^2O^3$. In some cases, the gold-salts are better adapted than the platinum-salts for determining the constitution of an organic base. But any well defined and stable salt in which the amount of acid or acid-radicle can be directly and accurately determined, will answer the purpose equally well.

To determine the rational formula of a compound which is neither acid nor basic, recourse must be had to its derivation and to its modes of decomposition. Thus indigo yields by analysis numbers corresponding to the formula, C^8H^5NO. By oxidising it with nitric acid, we obtain *isatin*, $C^8H^5NO^2$ (= indigo + O); and isatin treated with potash yields the potassium-salt of *isatic acid*, $C^8H^6KNO^3$. Now, as isatic acid exhibits the characters of a monobasic acid, this formula shows that it contains 8 atoms of carbon; and consequently isatin and indigo, which are related to it in the manner just mentioned, must also contain 8 atoms carbon. Substitution-products formed under the influence of chlorine, nitric acid, &c. are often of great use in determining rational formulæ. Thus the composition of mesitylol may be expressed empirically by either of the formulæ, C^3H^4, C^6H^8 or C^9H^{12}. But this body, under the influence of nitric acid, yields the three substitution-products, nitromesitylol, $C^9H^{11}(NO^2)$, dinitromesitylol, $C^9H^{10}(NO^2)^2$, and trinitromesitylol, $C^9H^9(NO^2)^3$, the composition of which is utterly irreconcilable with the formula, C^3H^4, or C^6H^8. Again, the composition of *naphthalin* might be expressed empirically by the formula, $C^{10}H^8$, or C^5H^4; but the existence of the compounds, $C^{10}H^7Cl$, $C^{10}H^6Cl^2$, $C^{10}H^5Cl^3$, $C^{10}H^5BrCl^2$, $C^{10}H^4BrCl^3$, and $C^{10}H^4Br^2Cl^2$, shows clearly that the higher formula is the true one.

When a compound is volatile without decomposition, its atomic weight may generally be determined by means of its vapour-density. In nearly all cases, the molecule of a compound in the gaseous state is supposed to occupy 2 volumes (Atomic Volume), in other words, the vapour-density is half the weight of the molecule, and the formula of the compound must be calculated accordingly. Thus the vapour-density of alcohol, as determined by Gay-Lussac, is 1·6133, referred to air as unity, or $\frac{1·6133}{0·0693} = 23·25$, referred to hydrogen as unity. The double of this number, or 46·5 is therefore the weight of the molecule. Now the composition of alcohol, as determined by elementary analysis, is C^2H^6O, and the weight of the molecule calculated from this formula is 46. The formula of alcohol is therefore C^2H^6O and not any multiple thereof.

II. Proximate Organic Analysis.

The knowledge of the ultimate elements of which an organic body is composed, is not sufficient to give a complete idea of its constitution, unless the substance under examination is a definite chemical compound, such as sugar, alcohol, albumin, &c. In that case, all the knowledge that we wish to obtain, or indeed that we can obtain regarding the constitution of the body, is derived from its elementary analysis, together with the study of its chemical reactions; but when a complex organ, as a leaf or a root, or a vegetable or animal fluid, such as the sap, milk or blood, is to be examined, it is necessary, before proceeding to the ultimate analysis, to separate the several definite compounds or *proximate elements*, of which the complex substance is made up; just as in examining a sample of granite, it is not sufficient to know the relative quantities of silicon, aluminium, potassium, oxygen, &c., which it contains, but we require also to know something of the manner in which these elements are grouped in the form of definite minerals; in other words, to ascertain what proportions of quartz, felspar, and mica enter into the composition of the rock.

The ultimate analysis of organic bodies is, as we have seen, reduced to a very complete system; there is indeed no element occurring in an organic compound which cannot be detected with certainty, and estimated quantitatively within very narrow limits. But it is otherwise with the proximate analysis. With regard to vegetable substances in particular, nothing more than a few general directions can be given. In the case of animal bodies, some progress has been made towards the establishment of a systematic course of qualitative analysis, but much remains to be done before the method can approach in regularity and exactness to the processes of mineral analysis.

The substance, whether vegetable or animal, solid or liquid, is divided into two parts, one for the determination of the inorganic, the other for that of the organic constituents. The former is dried and incinerated (see Ashes) and the ash examined by the processes of mineral analysis. The former, if the analysis is to be quantitative, and in some instances also for qualitative analysis, is dried at a temperature between 100° and 110° or 115° C., great care being taken not to let the heat rise too high, as organic bodies are very easily decomposed by heat. Some bodies must be dried at the ordinary temperature over sulphuric acid. Liquids are first evaporated in shallow basins over the water-bath, and the residue is then dried at a somewhat higher temperature.

The dried residue or the original substance, is then subjected to the action of various solvents, generally of ether, alcohol and water. Gerhardt recommends these solvents to be used in the order here indicated: this of course implies that the substance is previously dried. Ether dissolves especially fatty and waxy substances, resins and camphors; alcohol dissolves the same substances with less facility, but on the other hand, it dissolves many substances which are insoluble in ether; water dissolves saccharine, gummy and amylaceous substances, and salts of organic acids. Benzol, oil of turpentine, chloroform and sulphide of carbon, are also used as solvents. Vegetable alkalis are extracted by dilute sulphuric or hydrochloric acid; organic acids by dilute ammonia or potash. The solutions of vegetable acids, and of certain other substances thus obtained, are often treated with acetate or subacetate of lead, in order to precipitate the organic principles in the form of insoluble lead-salts, which are then decomposed by sulphuretted hydrogen. Acetate of aluminium and ferric acetate are also used as precipitants.

The solutions obtained in this way generally contain a mixture of proximate organic principles, which must be separated by fractional distillation, precipitation, saturation, or crystallisation: when crystals are obtained, it is mostly of great service to examine them by the microscope, in order to determine their form, and ascertain whether they are homogeneous.

Fractional precipitation with acetate of lead is much used for the separation of the higher terms of the fatty acid series, stearic, palmitic, acid, &c. The mixture of fatty acids is dissolved in alcohol; the solution is partially precipitated with acetate of lead; the precipitate is decomposed by sulphuric acid; the fatty acids thereby separated are redissolved in alcohol, and again partially precipitated; and this series of operations is repeated till the fatty acid thus separated shows a constant melting point.

The method of *fractional saturation* applied by Liebig to the separation of some of the lower terms of the fatty acid series, may also here be noticed. When valeric and butyric acids occur together in a liquid, their separation may be effected by half saturating the mixture with soda, and distilling. If the valeric acid is in excess, pure valerate of sodium is left behind, and a mixture of butyric and valeric acids distils over; if, on the contrary, the butyric acid is in excess, the residue contains butyrate as well as valerate of sodium: but the distillate consists of pure butyric acid. On distilling the residue with excess of dilute sulphuric acid, the two acids pass over together, and by partially neutralising the distillate with an alkali, and again distilling, a further separation may be effected. At each stage of the process, the less volatile acid (the valeric) displaces the more volatile, and one only of the acids is found either in the distillate or in the residue, according as the more or the less volatile acid predominates. When a mixture of acetic acid with butyric or valeric acid is treated in this manner, different phenomena present themselves, the acetic acid, though the most volatile, exhibiting the greater tendency to displace the other two and remain in the residue. This peculiar behaviour is due to the formation of an acid acetate of sodium, $C^2H^3NaO^2.C^2H^4O^2$, which is not decomposed by either of the other acids. Hence, if the mixture contains more acetic acid than is sufficient to form an acid acetate with the quantity of soda added, the excess will pass over together with the whole of the butyric or valeric acid present, the residue consisting of pure acid acetate of sodium; if, on the contrary, the quantity of acetic acid is less than sufficient to convert the whole of the soda into the acid acetate, pure valeric or butyric acid will pass over, and the residue will contain acid acetate of sodium, mixed with butyrate or valerate.

Volatile oils are separated by fractional distillation. The roots, seeds, leaves, &c., containing them are macerated in water and distilled, and the oils which pass over with the aqueous vapour, are separated mechanically from the watery distillate, and subjected to fractional distillation, the portions which distil at constant boiling points or between narrow limits of temperature being collected apart. Many volatile oils have the composition of aldehydes, and these are separated from mixtures containing them, by agitation with a saturated solution of acid sulphite of sodium, with which they form crystalline compounds.

In most cases, however, more information will be obtained concerning the best method of procedure in any particular case, by consulting the methods which are actually in use for separating special substances from complex mixtures in which they occur, than from any general rules: see for example the articles **Alkaloids (detection of)**, **Bone-oil**, **Cinchona-bark**, **Opium**, for the methods of separating alkaloids; the articles **Bile**, **Oleic Acid**, **Stearic Acid**, **Uric Acid**, &c., for the methods of separating acids; and the articles **Albumin**, **Glycerin**, **Sugar**, &c., for the methods of separating neutral bodies.

Examination of Animal Substances: Zoochemical Analysis.—The general directions just given for the proximate analysis of complex organic bodies, are for the most part equally applicable to vegetable and to animal substances: but the proximate principles of the animal body being less numerous than those of the vegetable kingdom, where distinct proximate principles occur in every natural order and in many individual species, it is somewhat easier to lay down a systematic course for the qualitative analysis of animal substances. The following is the method given by Gorup-Besanez, in the *Handwörterbuch der Chemie*, 2te Aufl. i. 984.

a. For liquids.—The physical characters must first be examined. Any turbidity or sediment occurring in the liquid is to be examined by the microscope for the detection of crystals, or bodies of any other definite form. An acid reaction of the liquid indicates the presence of free acids or of acid salts; an alkaline reaction, that of free alkalis, alkaline carbonates or phosphates (as in blood, blood-serum, and serous transudates, or of ammonia resulting from decomposition (as in urine). A coagulum forming spontaneously, after a while, in a liquid originally clear, generally consists of fibrin; it may also consist of organised bodies, a question to be decided by examination with the microscope.

The liquid, clarified, if necessary, by filtration or straining, is now to be examined as follows.

1. A portion of it is heated in a test-tube to the boiling point, acetic acid being added, before the boiling heat is attained, in sufficient quantity to produce a faint acid reaction, in case the liquid was originally neutral or alkaline.

a. If no distinct coagulum is formed, albumin is absent: pass on to (2).

b. A distinct coagulum or turbidity is produced: Divide the liquid into two portions. To one portion add a few drops of dilute hydrochloric acid. If the precipitate disappears, albumin is absent, but earthy phosphates are probably present. Look for them by the microscope or by chemical tests.

If the coagulum or turbidity does not disappear, add hydrochloric acid and heat to the boiling-point; if it dissolves gradually, with blood-red colour, albumin is present: for a confirmatory test, add a few drops of nitric acid to a small quantity of the original liquid.

N.B. If the coagulum formed by boiling the liquid, or the liquid itself, has a reddish-tinge, hæmatin and globulin may be present. The coagulum is then to be digested in alcohol containing sulphuric acid, and the liquid treated with the tests specially adapted to the discovery of those compounds.

2. The liquid in which no coagulum is produced by boiling, or the liquid filtered from the coagulum in the contrary case, may still contain the following albuminoïdal substances: paralbumin and metalbumin, casein and globulin.

If only a turbidity was produced on boiling the liquid, paralbumin or metalbumin may be present. Add acetic acid during ebullition; if the liquid then becomes turbid or deposits flocks, and yields a turbid filtrate, if it also gives a precipitate with ferrocyanide of potassium and nitric acid, and the last-mentioned precipitate is insoluble in excess of nitric acid, paralbumin is present. Then look for metalbumin with alcohol and ferrocyanide of potassium. If alcohol produces a precipitate soluble in a large quantity of water, but ferrocyanide of potassium produces no precipitate, metalbumin is present.

If the liquid remains perfectly clear on boiling, it may still contain the following albuminoïd substances and their derivatives; casein, globulin, glutin, chondrin, pyin, and mucus.

A sample of the liquid is mixed with ferrocyanide of potassium. If it remains clear, casein and globulin are absent: pass on to (3).

If a precipitate is formed, test for casein with solution of chloride of calcium and boiling, also with calf's rennet; for globulin, by observing whether a precipitate is formed by neutralising the solution after it has been made acid or alkaline.

3. To a portion of the liquid add acetic acid. If it remains clear, pyin, mucus, and chondrin are absent: pass on to (4).

A precipitate is formed: test the solution with corrosive sublimate. If no precipitate is formed, pyin is absent. The occurrence of a precipitate indicates the presence of pyin, which may be verified by tincture of galls and neutral acetate of lead. If the corrosive sublimate produces merely a turbidity, chondrin is perhaps present. Concentrate a portion of the liquid: the formation of a jelly indicates chondrin, the presence of which may be confirmed by its behaviour to alum and metallic salts.

4. The liquid in which acetic acid produced no precipitate may yet contain glutin. Concentrate a portion strongly, and leave it to cool: the formation of a jelly will then indicate glutin, which may be further tested with corrosive sublimate.

5. The original liquid—or of it contained albumin, the liquid freed from that compound by boiling—is concentrated by a gentle heat to $\frac{1}{2}$ or $\frac{1}{3}$ of its volume, then heated to boiling and left to cool.

If no precipitate forms, the liquid is probably free from urates: pass on to (6).

If a precipitate is formed, add acetic acid. If the hitherto amorphous masses are then seen under the microscope to assume the form of rhombic tablets, uric acid is present and may be further tested with nitric acid and ammonia.

A crystalline precipitate not altered by acetic acid points to the presence of sulphate of calcium, or phosphate of magnesium, which may be further submitted to microscopic and chemical examination. The precipitate, if crystalline, may also contain allantoin, tyrosin, hippurate of calcium, and benzoic acid. Microscopical examination and the general behaviour of the substance must then determine the further tests to be applied.

6. The concentrated liquid in which no precipitate is formed by boiling and subsequent cooling, or the liquid filtered from such a precipitate, is evaporated to a syrup on the water-bath, and left to itself for a considerable time.

If crystals gradually form, it is left to stand as long as they continue to increase. They may consist of creatine, creatinine, glycocoll, leucine, allantoin, taurine, sarcosine, inosite, alkaline hippurates, chloride of sodium and other inorganic salts.

It must in the first place be determined whether these crystals are organic or inorganic. In the former case, they must be tested especially for nitrogen, sulphur and phosphorus (p. 221), their chemical character determined as nearly as possible, and the further examination regulated accordingly. In the latter case, they must be treated by the methods of inorganic analysis. If they blacken when strongly heated, but also leave a fixed residue, they probably consist of an organic acid combined with an inorganic base: in that case, the fixed residue will effervesce strongly with acids.

7. The syrupy residue itself, or the liquid separated from the crystals which have formed in it is evaporated nearly to dryness, and the residue exhausted with alcohol of specific gravity 0·833.

a. A portion of the alcoholic solution concentrated and then diluted with water, is tested with nitric acid containing nitrous acid, for bile-pigment:—*b.* A second portion treated in like manner, is tested with sugar and sulphuric acid for the acids of bile:—*c.* A third portion is evaporated nearly to dryness, the residue dissolved in water, and the solution examined by Trommer's or Fehling's test for sugar:—*d.* A larger portion of the alcoholic solution is evaporated to a small bulk, the cooled residue treated with nitric acid free from nitrous acid, and the vessel immersed in ice-cold water or in a freezing mixture. A laminar crystalline precipitate exhibiting the micro-crystalline characters of nitrate of urea, indicates urea (care must be taken to distinguish it from nitrates of the alkalis). A crystalline precipitate appearing after some time, or more quickly after previous heating, indicates hippuric or benzoic acid, the presence of which must be verified by the microscope and by chemical reactions:—*e.* Mix a portion of the concentrated alcoholic extract with a syrupy solution of chloride of zinc: if a crystalline precipitate forms, it may contain creatine and creatinine: if no such precipitate appears after a considerable time, creatine is certainly absent:—*f.* The last portion of the concentrated alcoholic extract, which will exhibit a strong acid reaction, if any free acid is present, is to be heated with oxide of zinc, filtered hot, and a drop left to evaporate on a glass plate: if lactic acid is present, the characteristic club and tun-shaped crystals of lactate of zinc will be seen by examination with the microscope. The presence of lactic acid may be confirmed by preparing a pure salt of the acid from a larger quantity of the liquid.

8. The residue insoluble in alcohol may contain, in addition to inorganic and so-called extractive matters, uric acid, guanine, hypoxanthine, and albuminates not precipitated by boiling. It must be exhausted with water, which takes up casein, pyin, and extractive matters, together with soluble salts, then with dilute potash solution, which dissolves uric acid, hypoxanthine, and guanine, and lastly, with dilute hydrochloric acid. What then remains may contain albuminates which have become insoluble, mucus, and perhaps also silica. All these substances must be further looked for by special tests.

9. Part of the original liquid is evaporated to dryness, and the residue, pulverised if possible, is exhausted with ether. The ethereal extract, chiefly containing fats in solution, is evaporated and further examined (see FATS and GLYCERIDES). The residue insoluble in ether is incinerated, and the ash examined by the methods of inorganic analysis.

β. Tissues and Organs.—In the analysis of animal tissues, it is absolutely necessary to operate with considerable quantities of material, not less than 20 pounds; otherwise a very tedious investigation may be gone through without any satisfactory result.

The tissue is first carefully comminuted and completely exhausted with cold water; the extract is freed from albumin by boiling, and to the filtered liquid a concentrated solution of caustic baryta is added as long as any precipitate or turbidity is produced. The precipitate may contain phosphate of barium, phosphate of magnesium, sulphate of barium, uric acid, and hypoxanthine. The filtrate is evaporated to a syrup over the water-bath, care being taken to remove any mucous films like casein that form during the evaporation. These generally consist of carbonate of barium or phosphate of magnesium, but may also contain uric acid, hypoxanthine, or barium-salts of organic acids; they must, therefore, not be thrown away. As soon as the filtrate is concentrated to the consistence of a thin syrup, it must be left to evaporate spontaneously. If small short colourless prisms form in it, they probably consist of creatine; as soon as they appear to be completely deposited, they are to be separated from the mother-liquor, recrystallised, and submitted to further examination.

The mother-liquor is then further evaporated, and mixed with small portions of alcohol, till a milky turbidity is produced, after which the mixture is left to itself for a few days; if granular, laminar, or needle-shaped crystals form in it, they may contain, besides creatine and phosphate of magnesium, inosate of potassium and inosate of barium. To obtain the inosic acid, dissolve the deposit in hot water, add chloride of barium, purify the inosate of barium which separates by crystallisation, and separate the inosic acid by precipitation with dilute sulphuric acid.

The liquid separated from the deposit of inosates is now to be mixed with a fresh portion of alcohol, whereupon it generally separates into two layers, the lower being syrupy, the upper more mobile. The upper layer is decanted, and the lower is mixed with an equal volume of ether, which generally causes a fresh separation. The lower stratum thus formed may contain alkaline lactates, inosite, and salts of the volatile fatty acids; the upper, creatinine and leucine. The ether-alcoholic liquid is evaporated and left to crystallise. If the residue gradually deposits fine laminated crystals, dilute it with a little alcohol, filter off the mother-liquor, and treat the crystals with boiling alcohol; they may contain creatine and creatinine. The creatine separates immediately as the filtrate cools; the creatinine crystallises from the mother-liquor.

The heavy syrupy liquid mixed with the mother-liquor of the creatine and creatinine is supersaturated with dilute sulphuric acid, in order to precipitate all the baryta, and the filtrate is distilled to obtain the volatile acids. The residue of the distillation, if shaken up with ether, may perhaps yield lactic and succinic acids.

The residue of the distillation, after being freed from these acids, is mixed with strong alcohol, till it becomes turbid, and left at rest. Sulphate of potassium then crystallises out, and on repeatedly adding fresh portions of alcohol, more sulphate of potassium, together with inosite, which must be separated from the sulphate of potassium, as far as possible by mechanical means, and then by recrystallisation from a small quantity of warm water. To obtain hypoxanthine and uric acid from the baryta-precipitates, viz. that which separated in films at the beginning of the process, and that which was produced by adding sulphuric acid to separate the volatile acids treat the united precipitates with boiling potash-ley, filter, acidulate with hydrochloric acid, redissolve the resulting precipitate in potash, and add sal-ammoniac. Uric acid is then precipitated as urate of ammonium, while hypoxanthine remains in solution, and may be obtained by evaporation as a yellowish-white powder.

If the filtrate from the coagulum of albumin, after being evaporated to a syrup, does not yield any well developed crystals, but after standing for some time, masses having a crystalline aspect, soft and unctuous to the touch, and appearing under the microscope as yellowish refracting spherules, the presence of leucine may be suspected. These masses are then to be separated from the mother-liquor, which, after standing for a longer time, deposits more of them, and the entire product strongly pressed between porous tiles and purified by repeated crystallisation from boiling alcohol. If tyrosine is present, it covers the filtrate, after it has been freed from the albumin-coagulum and evaporated, with numerous stellate groups of slender needles, which for the most part remain undissolved when treated with alcohol. They may be dissolved in boiling water, whence they separate on cooling,—purified by solution in hydrochloric acid, with addition of acetate of potassium, and boiling,—and then further examined.

The mother-liquors from the leucine and tyrosine deposits are examined as above for volatile acids, lactic acid, succinic acid, inosite, &c.

Another process for the examination of animal tissues is given by Städeler and Cloëtta:

The extracts obtained by maceration and pressing are boiled with a few drops of acetic acid to coagulate albumin and colouring matter of blood, and the strained liquid, after being evaporated over the water-bath to $\frac{1}{10}$ of its bulk, is precipitated with subacetate of lead. The precipitate, which may contain uric acid and inosite, is collected on a filter and washed; the filtrate is freed from excess of lead by sulphuretted hydrogen, and evaporated to a syrup; the residue, which generally contains alkaline acetates, is freed from these compounds by digestion in cold weak alcohol; sulphuric acid diluted with alcohol is then added as long as a precipitate of alkaline sulphates continues to form; and the excess of sulphuric acid is removed by careful addition of baryta-water. The clear filtrate evaporated till it no longer becomes permanently turbid when mixed with an equal volume of absolute alcohol, is heated till the turbidity disappears, and then left at rest. Any crystals which separate must be further examined: they may consist of creatine, but also of tyrosine and taurine, which last compound has lately been found by Cloëtta in the tissue of the lungs. The mother-liquor of the crystals, if carefully evaporated to a smaller bulk, deposits any leucine that may be present.

The precipitate produced by subacetate of lead is washed, suspended in water, and decomposed by sulphuretted hydrogen. If the liquid filtered from the sulphide of lead deposits, after some time, small white crystalline grains, exhibiting under the microscope the forms of uric acid, they must be collected and examined for uric acid by the murexide test (URIC ACID). The liquid filtered from the uric acid is evaporated over the water-bath, till a sample mixed with alcohol becomes permanently turbid. The entire liquid is then mixed with an equal volume of alcohol, and warmed till the turbidity disappears. If after some days, a deposit forms on the bottom and sides of the vessel, consisting of crystalline masses, which, when recrystallised from water, form rhombic prisms insoluble in alcohol and ether, having a pure sweetish taste, and leaving no residue when burnt, inosite is probably present, and must be sought for by other tests. [For further details, and for the quantitative analysis of animal substances see Lehmann, Lehrb. d. physiolog. Chem. 2te Aufl. Leipzig, 1853; Heintz, Lehrb. d. Zoochemie, Berlin, 1853; Robin et Verdeil, Traité de Chimie anat. et physiol. Paris, 1858; Gorup-Besanez, Anleitung zur zoochem. Analyse, 2te Aufl. Nürnberg, 1854.]

ANALYSIS (VOLUMETRIC) of LIQUIDS and SOLIDS. The method usually employed by chemists to determine quantitatively the constituents of a mixture, consists in separating them out one after the other, either in the pure state, or in the form of some compound of known composition, and weighing the products. Every one who has occupied himself with such separations knows how much time they usually require; indeed the value of an analytical result is very often much less than that of the time and trouble spent upon its determination. We are indebted to the sagacity of Gay-Lussac for the introduction of a new principle in analytical chemistry, which in many instances obviates the inconvenience mentioned. This consists in submitting the substance to be estimated to certain characteristic reactions, employing for such reactions liquids of known strength, and, from the quantity of the liquid employed, determining the weight of the substance to be estimated by means of the known laws of equivalence. Let us, for example, consider the problem which suggested to Gay-Lussac the idea of this method. Suppose it be required to determine the amount of silver in an alloy of silver and copper. The older analytical method consists in dissolving a weighed quantity of the alloy in nitric acid, precipitating the silver as chloride by the addition of hydrochloric acid, then filtering, washing, fusing, and weighing the resulting chloride of silver. From the known fact that chloride of silver contains $\frac{108}{143{\cdot}5}$ of its weight of silver, the amount of silver in the alloy is calculated. The same result is evidently obtained by preparing a solution of chloride of sodium of known strength, and ascertaining how much of the solution is necessary and sufficient to precipitate the silver as chloride of silver from a solution of a weighed quantity of the alloy in nitric acid. The weight of the precipitated silver may be determined from the amount of the chloride of sodium employed; because it is known that 58·5 parts by weight of chloride of sodium are exactly sufficient to convert 108 parts of silver into chloride of silver.

The liquid reagents of known strength employed in determinations of this nature are called "standard solutions." The amount of standard solution employed in a determination may be estimated either by weight or by volume; but inasmuch as the latter method has been found easier of application, it is now universally employed; and hence the method of analysis based upon the use of standard solutions is called "volumetric analysis." At first glance it would seem that nearly all analytical methods based upon weight might be transformed into processes by volume, as in the case of the silver determination above quoted. This is, however, not always possible. A reaction to be applicable in volumetric analysis must satisfy two conditions. (1.) It must not occupy much time; precipitations, for instance, which take place gradually are at once to be rejected. (2.) The termination of the reaction must be recognisable with ease and certainty. Hence the number of possible volumetric processes is much limited. On the other hand numerous reactions inapplicable in weight-analysis furnish excellent means for volumetric determinations.

It is proposed in this article to give a short introduction to volumetric analysis, and for this purpose the subject will be divided into three parts:

I. Description of the necessary apparatus.
II. General rules for the preparation of standard solutions.
III. Description of the most important volumetric methods as yet discovered.

I. *Apparatus: description, use, and verification.*—Besides the apparatus necessary for ordinary chemical operations, such as beakers, basins, &c., the performance of volumetric analysis requires: (1.) a delicate balance and weights. (2.) Graduated glass vessels for the measurement and preparation of the standard solutions. A balance is necessary for the preparation of the standard solutions, and for weighing the substances to be analysed. A good analytical balance capable of weighing 100 grammes, is quite sufficient for both purposes. To those who have many volumetric analyses to perform, a small light sensible balance with short arms is of great use. Such balances admit of more rapid weighing than can be obtained by the ordinary laboratory balances.

The absolute magnitude of the units of weight and measure adopted, may of course be chosen at pleasure. But the French decimal system of weights and measures offers so many advantages, chiefly on account of the simple relation which it establishes between the units of measure and weight, that its employment in the sequel in all data of weight and measure needs no justification.

In order to be able to measure the standard solutions accurately, certain precautions are to be observed which we will now proceed to consider more particularly.

When an aqueous solution is poured out of a vessel, the vessel is, as is well known, never completely emptied; a small portion of the solution remains always upon the the sides, even after the vessel has been long held in an inclined position. In using a measure for liquids we must, therefore, be careful to note whether the *dry* vessel, when filled up to a certain line, holds the required volume, or whether such volume is delivered from the vessel when it is emptied in a certain manner. In the first case the vessel is said to be graduated for the contents; in the second for delivery (*à l'écoulement*). The reading off is performed by bringing the eye and the surface of the liquid into one horizontal line, and noting what division of the volumetric instrument is opposite to the liquid surface. Now aqueous liquids which are enclosed in cylindrical glass vessels, always show a concave surface, which is the more strongly curved the narrower the vessel. But a curved surface is of course opposite to *many* points of the scale at once. In order to avoid the ambiguities which are here introduced a definite method of reading off must be invariably adopted. The following has been found practically the best. A small piece of black paper is fastened a few millimetres below the surface of the liquid by means of a caoutchouc ring; the instrument is brought into an exactly vertical position, one eye is closed, and the other brought to the right elevation. The meniscus then appears by transmitted light, sharply bounded below by a black line, by means of which it is easy to see with what point of the scale the former coincides (see ANALYSIS OF GASES). In order to ensure a fixed point of sight the eye, the meniscus, and a distant horizontal line, of about the same elevation as the eye, are either brought into one horizontal line, or the instrument is placed at a short distance before a vertical strip of mirror, and the eye is brought into such a position that the image of the pupil and that of the meniscus may coincide as nearly as possible: the scale is then read off.

It must be mentioned that the volume of every body varies with the temperature, and that consequently the divisions on a measure for liquids, as well as the strength of a standard solution, are applicable for one temperature only. The expansion of the glass is so small that it may be always neglected in volumetric analyses. A glass vessel, for instance, which holds a liter at 15° C. contains at 15° ± 10°, one litre ± 0·27 c.c.: now 0·27 c.c.; are only the $\frac{1}{4000}$ of a litre. The expansion of liquids is greater, and must be taken into account in exact experiments.

This is especially to be attended to when volumetric instruments are to be graduated by determining the weight of water which they hold. In this case the correction for the expansion of water by heat is not the only one to be made. Since one gramme is by definition the weight in vacuo of one cubic centimetre of water at + 4° C., the volume of a given quantity of water in c.c. is never expressed by the same number as its *apparent* weight in grammes, even at + 4° C. There is of course no necessity for employing the *real* cubic centimetre in volumetric analyses; but, as everything connected with weights and measures should be as precise as possible, we think it advisable to use the words litre, cubic centimetre, &c., in their strict sense.* We therefore give the following table, by means of which the apparent weight of a certain required volume of water may easily be found.

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* There are, even in scientific researches, cases in which *absolutely* correct measures must be employed; for instance, 1 litre of air of 0° C. has the weight of 1·293 grms., only when its tension is equivalent to the pressure of a mercury column 0·76 *real* metres high, the litre being the volume of a quantity of water of 4° C., which balances *in vacuo* the kilogramme employed.

The weight of 1000 c.c. of water of t° C. when determined by means of brass weights in air of t° C. and of a tension of 0·76 metres, is equal to $1000 - x$ grms.

t°	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
x	1·25	1·20	1·15	1·13	1·12	1·12	1·14	1·16	1·21	1·27	1·34	1·43	1.52	1·63	1·76	1·89

t°	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31
x	2·04	2·20	2·37	2·55	2·74	2·95	3·17	3·39	3·63	3·88	4·13	4·39	4·67	4·94	5·24	

When the barometer stands at $76 \pm n$ centim., every x is to be replaced by $x \pm 0{\cdot}014\,n$. The variations of atmospheric pressure may however be neglected, unless a very great degree of exactness is required.

If the strength of a standard resolution is known for one temperature, the strength corresponding to another temperature can only be calculated, if the rate of expansion by heat of the liquid is known. It would lead to entirely wrong results if such calculations were founded on the known expansion of pure water, as experiment has shown that even weak solutions of salts and acids expand far more than water (see Gerlach "Specifische Gewichte der Salzlösungen, &c.," Freiberg). As long as the expansion of the commonly used standard solutions is not directly determined, it is advisable to estimate the strength of such solutions not only by volume, but also by weight, which is easily done by weighing a known volume of the liquid immediately after its strength has been determined. The ratios of the *weight* of the solution to the weight of active substances in it, is of course independent of temperature.

It is a matter of course that such corrections are appropriate only where the errors from other sources are not greater than the corrections themselves.

We may now proceed to describe the separate instruments.

1. *Pipettes.*—Glass vessels of forms shown in *figs.* 40* and 41, provided with a single mark upon the narrow neck, and which are only graduated for delivery. In using them, they are filled, at a little above the mark, by suction, and then closed above with the forefinger of the right hand. The lower point is brought in contact with a wet piece of glass; the liquid is allowed to flow out, by very gentle displacement of the finger, as far as the mark; and the finger is then removed, to allow it to run out into the vessel employed. The drop of liquid in the point of the pipette is to be kept in exactly the same conditions as during the marking of the pipette; *i. e.* it is either totally neglected, or it is partly removed by holding the point against the wet side of the glass, or it is to be blown out entirely. If the same method of evacuation be always faithfully followed, we may assume that, with all thin liquids, equal volumes remain adhering to the sides of the vessel.

It is convenient to be provided with such pipettes containing 100 c.c., 50 c.c., 20 c.c., 10 c.c., and 5 c.c. Pipettes of 10 and 5 c.c. may conveniently have the form of *fig.* 41, larger ones the form of *fig.* 40*. It seldom happens that we have to make pipettes ourselves, as they may be bought at a low price; but they should always be verified. This is easily done by filling them with water of a known temperature, pouring this into a tared flask, and weighing. The volume of the water may then be found from its weight by means of the table above given.

2. *Pipettes* which are divided throughout their whole length and graduated for delivery. It is sufficient to have one of 50 c.c., which is divided in half c.c. (*fig.* 42), and several of 2 to 3 c.c., divided into $\frac{1}{10}$ c.c. (*fig.* 43).

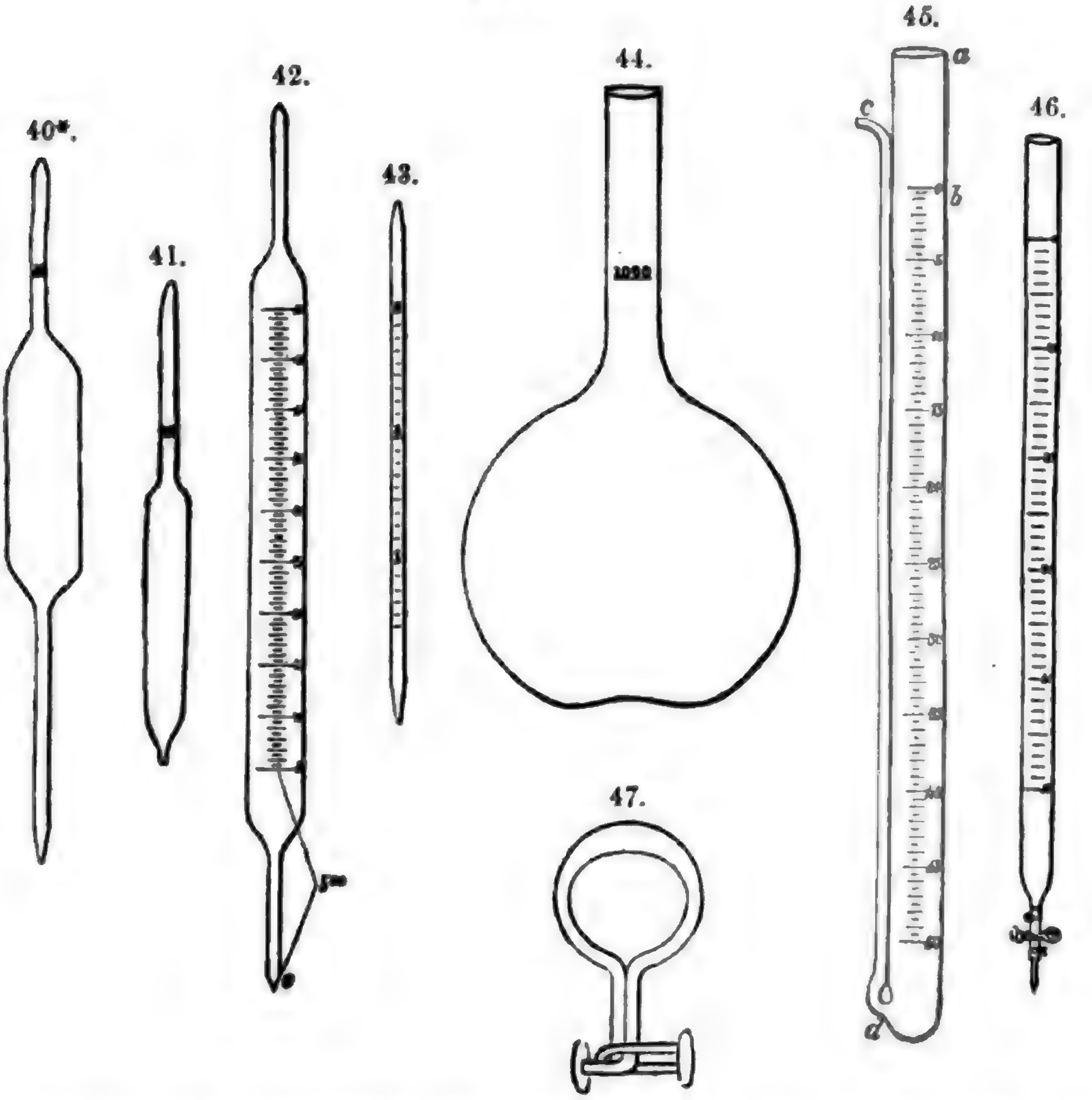
3. *Flasks*, graduated for the contents (*fig.* 44), in various sizes, from $\frac{1}{10}$ litre to 5 litres. They may be easily made by making an arbitrary mark upon the neck of the flask, and then measuring the volume by pipettes. It is more exact to weigh the contained water. It is convenient if, but not absolutely necessary that, the volumes of these flasks should be whole numbers, such flasks being used only for the preparation of standard solutions.

4. For measuring the liquids used in an analysis the *burette* is most generally employed. This is an ingenious instrument invented by Gay-Lussac. Upon a glass tube (*fig.* 45) about 16 – 18 mm. wide and 30 centim. long, a narrow tube is fused at *d*, carried up *close* along the wide tube to about 2 ctm. from its upper end, and there (at *c*) bent and cut off in the manner shown by the figure. The divisions of $\frac{1}{2}$ c.c. begin about one ctm. below *c*, and the instrument is graduated "for delivery." In using the burette it is washed out with some of the standard solution, then filled to 0; the point *c* is slightly greased, and the required quantity of liquid is poured out of the narrow tube.

After some practice it is easy to allow the liquid to flow out either in a stream or in drops. The volume must not be read off before the surface has attained a constant height. Tenths of cubic centimetres may, after some practice, be easily judged of by the eye in burettes graduated to half cubic centimetres. It is erroneous to suppose that greater accuracy is attained by employing narrower tubes. The gain in accuracy due to the increased distance of the divisions is lost, because in narrower tubes, the meniscus is less sharply defined, and the quantity of liquid adhering to the sides is less constant. A burette of the dimensions given, contains 50 to 60 c.c., an amount more than sufficient for most analyses: larger burettes are inconvenient. If more than 50 c.c. liquid are required in analysis, the greatest portion is measured off in a pipette. (40*.) and the remainder added from the burette. In cases where greater accuracy is required than can be attained by the burette, the latter is replaced by the use of several pipettes.

Mohr has substituted for Gay-Lussac's burette a simple divided tube (*fig.* 46), provided below with a caoutchouc tube, which is closed by a spring clamp (*fig.* 47) (*Quetsch-Hahn*) made of brass wire. Where a great number of analyses of the same kind have to be performed, Mohr's burette is much to be preferred to Gay-Lussac's. In scientific laboratories, however, where a greater diversity of analyses occur, the old form is preferable, inasmuch as caoutchouc is acted upon by some solutions which are frequently employed.

Figs. 40*—47.



The verification of a burette is performed either by the balance or by the pipettes described in (1).

II. *Preparation of the Standard Solutions.*—Standard solutions may be divided into (1) such as are immediately prepared by weighing a substance of known composition, dissolving it and diluting to a certain volume; (2) such as are prepared by approximate mixture and subsequent exact analysis. The preparation of the first kind requires no description. The preparation of the second may be effected by a kind of successive approximation, which is best described by an example.

Let it be required to prepare a standard solution of sulphuric acid containing t grammes of hydrate of sulphuric acid SO^4H^2 in 1 litre. The table given by Bineau of the relation between the specific gravity and strength of sulphuric acid affords the best means for determining the strength to the first approximation. Pure sulphuric acid (monohydrate, SO^4H^2) is diluted with about its own weight of water; the mixture is allowed to cool, and its specific gravity is quickly and accurately determined by measuring 100 c.c. in a pipette, weighing this, and dividing the weight (in grammes) by 100. If the temperature be observed, the percentage of monohydrated sulphuric acid (p) may be determined by the table, to within a hundredth of its true value. According to the result of this determination every $\frac{t}{p}\,100 = q$ grms. of the solution are diluted with water up to 1 litre. From Bineau's table (see SULPHURIC ACID) the specific gravity (S) of the required solution may be seen. To every q grms. of acid, $1000\,S - q = w$ grammes of water have to be added. An analysis performed with this mixture generally shows that it contains not t but t^1 grms. in 1 litre. Two cases are now possible:

(1) t^1 is greater than t. It is clear that the quantity t^1 of sulphuric acid contained in 1 litre is sufficient for $\frac{t^1}{t} = (1 + \Delta)$ litre. With every 1 litre of the mixture, Δ litre of water must be mixed, in order to bring it to the right strength. (2) t^1 is less than t. From t^1 grms. of sulphuric acid only $\frac{t^1}{t} = (1 - \Delta)$ litre of standard solution can be formed. Hence 1 litre of our mixture may be regarded as a mixture of $(1 - \Delta)$ litre of right standard solution and Δ litre of water. Hence to every litre of the solution as much of the acid of p per cent. must be added as is sufficient to form the right standard solution, with Δ of litre water; and since by mixing q grms. of the p per cent. acid with w grms. of water, we had obtained a mixture of nearly the right strength, it follows that the quantity of strong acid which must be added to every litre is $\left(\frac{1000\,.\,\Delta}{w}\,q\right)$ grammes, neglecting an error which need not be considered, if Δ is a small fraction.

After performing these operations, we must determine by experiment how nearly we have arrived at the required strength, and, if necessary, make a second correction. If the corrections required are great, it will be almost invariably found, on performing the analysis, that the strength required has not been exactly attained, however carefully the mixture of the liquids may have been made. This is the case even if the above described approximate synthesis is replaced by a theoretically exact one, this cause of the inaccuracy being, that in the measurement and mixture of large quantities of liquids, small errors of measurement and losses are difficult to avoid, and that the contraction of the mixture has been neglected. If, on the other hand, the solution to be corrrected is already so nearly right, that its strength differs by only 1 or 2 *per cent.* from that which is required, the result will be satisfactory, even if the volume of the liquid taken was only approximately determined, provided the analysis was performed accurately, and the measurement of the small quantities of water or acid which were added, were made with sufficient care.

If, for instance, we consider the case (1) and assume that the volume of the acid to be corrected was found to be n litres, while in fact it was $n\,(1 + \alpha)$ litres, the quantity of water to be added would then be, not $n\,\Delta$ litres but $n\,\Delta\,(1 + \alpha)$. The resulting volume of the mixture would accordingly be too small by $n\,\Delta\,(1 + \alpha) - n\,\Delta = n\,\Delta\,\alpha$. If, for instance, it is found that $\alpha = \frac{1}{50}$, which seldom occurs, if moderate care is employed, and $\Delta = \frac{1}{100}$, then the volume of the mixture would be $n\,\frac{2}{1000}$ litres too small, and consequently the amount of sulphuric acid in 1 litre would be too large by about $\frac{1}{5000}$ of its actual quantity. Similar considerations are applicable to case (2), and lead to the conclusion that in the preparation of large quantities of liquids, according to the method just described, large measures accurately divided are not necessary. Such processes are conveniently performed in large cylindrical bottles, which are divided down the side with divisions corresponding to entire decilitres. As the liquid in such cases is not transferred from one vessel to the other till it is quite prepared, loss is easily avoided.

The strength of a solution is best noted by giving the number (n) of gramme-atoms of the active substance which it contains in 1 litre. By "gramme-atom" we understand a number of grammes equal to the atomic weight of the substance ($H = 1$), for instance, 108 grammes silver, 28 iron, 35·5 chlorine, &c. It is clear that the calculations are hereby simplified. For instance, 1 litre of solution of silver, containing *n* atoms (= *n* × 108 grms.) of silver exactly precipitates *n* × 35·5 grms. of chlorine, *n* × 80 grms. of bromine, *n* × 127 grms. of iodine. It is also evident that calculation will be facilitated by making *n* a small number. If it can be done without loss of time, it is in fact advisable so to adjust the strength of the standard solution that $n = 1, \frac{1}{2}, \frac{1}{10}$, &c.

It is of the highest importance that the standard solutions should remain of constant strength. To ensure this condition, they must be carefully protected from evaporation and other hurtful influences. Large quantities may be preserved in bottles of 1 or 2 litres capacity, provided with well ground stoppers. Bottles which are not in daily use should have have their stoppers greased and bound over with bladder or sheet caoutchouc.

III. *Description of the most important Volumetric processes hitherto employed.*—Among the many volumetric methods hitherto discovered, those only are of general scientific interest by help of which the analysis of a whole series of bodies can be made with one, or at least, a few standard solutions. These alone will be more particularly considered here. For the many methods applicable in special cases, reference must be made to the several articles of this work.

Volumetric determinations may be classified as follows, according to the principles on which they are based: —

1. *Analysis by Precipitation.*—The quantity of the substance to be determined, is derived from that of the reagent required to separate it out in an insoluble state.

2. *Analysis by Saturation.*—The quantity of a base or an acid is measured by the quantity of acid or base which is necessary to convert it into a neutral salt.

3. *Analysis by Oxidation and Reduction.*—The quantity of substance to be determined is found by the quantity of chlorine, bromine, iodine, or oxygen to which it is equivalent (regarded as oxidant), or by the quantity of chlorine, bromine, iodine, or oxygen which it requires to pass from a lower to a higher stage of oxidation.

1. ANALYSIS BY PRECIPITATION.—Of the numerous methods belonging to this division, we will here consider those only which depend upon the insolubility of the combinations of silver with the halogens (chlorine, bromine, iodine, cyanogen).

If the neutral or slightly acid solution of a chloride, bromide, iodide, or cyanide, is mixed with a solution of nitrate of silver, it is well known that an insoluble chloride bromide, &c., of silver is precipitated, while a nitrate remains in solution. For instance

$$NO^3Ag + ClNa = ClAg + NO^3Na.$$

All these silver precipitates have the common property of forming, on violent agitation, a curdy mass which rapidly subsides. Hence it is possible to recognise exactly the point at which the precipitation is completed. The reactions mentioned may, therefore, be employed, on the one hand, to determine chlorine, bromine, &c., by means of a standard silver solution, and on the other, to determine silver by standard solutions of chlorides, bromides, &c.

Special processes for the determination of Hydrochloric Acid and Chlorides.

Necessary reagents.

1. Chemically pure silver in the form of foil or wire.

2. A silver solution (nitrate) containing $\frac{1}{10}$ gramme-atom (10·8 grm.) silver in 1 litre. It is easily prepared by dissolving 10·8 grm. of silver in excess of nitric acid and diluting to 1 litre.

3. A solution of $\frac{1}{100}$ grm.-atom = 1·08 grm. silver in 1 litre.

4. A solution of chloride of sodium of $\frac{1}{10}$ grm.-atom (= 5·85) in 1 litre.

a. 5·85 grm. pure recently fused chloride of sodium is dissolved in water and diluted litre.

b. A solution of chloride of sodium saturated at ordinary temperatures, has a composition almost independent of the temperature: it contains in 1 litre, 318·4 grm. of NaCl. 18·37 c.c. $\left(= \frac{1000 \times 5{\cdot}85}{318{\cdot}4}\right)$ diluted to 1 litre, gives accordingly the standard solution required.

The chloride of sodium solution must, if properly prepared, be exactly equivalent to the silver solution (2). We must never neglect to try whether this is really the case by the method to be described below, and if necessary to make the proper corrections.

5. A solution of chloride of sodium containing $\frac{1}{100}$ grm.-atom in 1 litre = 0·585 grm.

6. Freshly prepared chloride of silver: this is obtained by mixing equal volumes of (2) and (4), shaking vigorously and pouring off the clear liquid.

Performance of the Analysis.—Let us at first assume that we have an approximate knowledge of the amount of chlorine in the substance to be examined. In this case a weighed quantity is introduced into a bottle of clear glass with a well-fitting stopper, dissolved in water or nitric acid, and the previously calculated quantity of strong solution of silver (2) is added from a pipette. The quantity of substance, and that of the water employed in its solution or dilution, are to be so taken that 100 c.c. of the mixture may contain 0·4 grm. to 1 grm. silver, and less than about 3 gms. of the dissolved salt. If a mixture has to be examined which is poor in chlorine, this relation is no longer possible. In such cases, enough freshly precipitated chloride of silver (6) must be added to bring the quantity of silver present up to that mentioned. Small quantities of silver-precipitates disseminated through much liquid do not evince that adherence and consequent tendency to subsidence which is necessary for the accurate performance of this mode of analysis. Solutions which are poor in chlorine, such as mineral waters, must be concentrated by evaporation previous to analysis. It is also advisable in such cases not to employ a standard solution of silver, but to weigh metallic silver and dissolve it in a minimum of nitric acid.

The mixture obtained as above is now to be violently and continuously shaken, till it has lost its first milky appearance, and forms a mixture of curdy chloride of silver in the midst of a clear solution. A speedy clarification is evidence of an excess of silver; slow subsidence indicates the reverse.

As soon as the chloride of silver has sufficiently subsided, ½ c.c. of strong solution of silver must be added, in order to determine whether chlorine is still present in the solution. If no precipitation occurs, the ½ c.c. silver solution is neutralised by the addition of ½ c.c. solution of chloride of sodium; the liquid is then shaken, and ½ c.c. of solution of chloride of sodium being added shows whether silver is in solution. Let us assume, for example, that the addition of the chloride of sodium has shown the presence of silver in considerable quantity. The amount of solution of chloride of sodium, which is exactly equivalent to this, cannot of course be known; but in every case we are sure of the existence of some maximum value (V c.c.) which certainly includes it. $\frac{V}{2}$ c.c. of chloride of sodium solution is then added, the mixture is shaken, and ½ c.c. of the same solution being added shows whether the precipitation with the first quantity was complete or not. In the first case, $\frac{V}{4}$ c.c. of silver are added; in the second $\frac{V}{4}$ c.c. of chloride. In both cases, the completion of the precipitation is tested by the addition of ½ c.c. of test solution. By continually adding half the possible maximum of the necessary reagents, we soon arrive at a point when less than ½ c.c. of one of the two solutions is present in excess. When this point is arrived at, cubic centimetres are added singly of the weaker ($\frac{1}{100}$ atomic) solutions, until the last cubic centimetre leaves the liquid quite clear, This last c.c. is not at all considered, and the one preceding it is considered only of the value of ½ c.c. In this way, a result is obtained, the error of which corresponds to less than ½ c.c. of the weak standard solution. It is easily seen that a systematic procedure like that given is quite essential, in order to arrive quickly at a result; by planless addition of standard solutions, we may lose much time without arriving at any result. As long as $\frac{1}{10}$ atomic solutions are added, it is scarcely necessary to wait for a complete subsidence of the precipitate previously formed. The white cloudy freshly precipitated chloride of silver is easily distinguished from the previously precipitated, violet-coloured, and coagulated chloride. As soon, however, as we begin to work with $\frac{1}{100}$ atomic solutions, we must always wait for the complete clarification of the liquid before adding a fresh quantity of solution. Weak precipitations are best seen by holding the vessel against the light, with a piece of black paper obliquely behind it. The precipitation can be considered complete only when the last cubic centimetre of solution gives no more turbidity after ½ to 1 minute's standing.

Those who make such analyses for the first time, will do well to place in several flasks some chloride of silver (6) and 100 c.c. water, then add to the several flasks ¼, ½, 1, 2 milligrammes of silver; shake, and after subsidence add to each flask 1 c.c. of the $\frac{1}{100}$ atomic solution of chloride of sodium. By this means the judgment is greatly assisted in the subsequent actual reactions.

Experience has shown that it is not expedient to work with less than ½ grm. of silver at once, and that no greater accuracy is obtained by adding less at once than 1 c.c. of the $\frac{1}{100}$ atomic solution; the termination of the reaction is thereby only rendered more indistinct.

If it be desired to arrive at the utmost accuracy in such determinations, a second analysis may be made by dissolving 1 grm. or more of silver in nitric acid, adding the quantity of substance necessary for its precipitation, as found from the previous analysis, and completing the precipitation by means of the $\frac{1}{100}$ atomic solution. The determination of atomic weights, performed in this way by Marignac and Pelouze, shows to what great accuracy the process may be brought.

It has been hitherto assumed that the amount of chlorine in the substance is approximately known. If this is not the case, the definite determination must be preceded by a trial upon a small quantity of the substance. The more exact such trial is made, the quicker will be the performance of the final determination.

The calculation of the analysis is very simple. The number of atoms of silver, diminished by the number of atoms of chloride of sodium, added as standard solution, is equal to the number of chlorine-atoms contained in the substance.

That which is here described for chlorine is applicable, *mutatis mutandis*, to bromine, iodine, and cyanogen.

The determination of silver by means of chlorine also follows immediately from the above, and requires no further explanation.*

2. Analysis by Saturation.—All methods belonging to this division depend upon the fact that potash, soda, ammonia, baryta, strontia, and lime combine easily and directly with acids, and that the corresponding carbonates are fully decomposed in contact with stronger acids, with evolution of carbonic acid. The solutions of the neutral salts which the above named bases form with strong acids are without action upon litmus, while the smallest excess of acid or alkali is immediately detected by its reddening or blueing that vegetable colour.

Reagents.—1. Pure anhydrous *monocarbonate of sodium*. If this salt be kept ready prepared in powder, it must always be ignited before use. Carbonate of sodium, fused in a platinum crucible, and cast in slabs, is less hygroscopic, but its use must be avoided, since Scheerer has shown that carbonate of sodium loses on fusing a considerable part of its carbonic acid.

2. Standard solution of *hydrochloric acid*, containing nearly or exactly 36·5 grms. HCl (1 atom) in 1 litre. This may be prepared in several ways.

a. The most exact method is to determine the specific gravity of a sample of concentrated pure hydrochloric acid, deduce its strength by means of Ure's table† (see Hydrochloric Acid, under Chlorine), add the proper amount of water and determine *exactly* the strength of the mixture by means of silver solution, as described in a preceding paragraph.

b. A concentrated acid, whose strength is approximately known from its specific gravity, is so far diluted that it contains, as nearly as can be effected by this means, 20·2 *per cent.* of HCl. If the liquid so obtained be quickly boiled in a narrow necked flask, or in a retort in contact with platinum (not in an open basin), a time soon arrives after which hydrochloric acid and water evaporate in the same proportion in which they are contained in the residue. If about one half be evaporated we may be certain that the point mentioned is attained. The percentage strength of the residue depends upon the contemporary barometric pressure, according to the following table, derived from experiments made on this subject by Roscoe and Dittmar. (Chem. Soc. Qu. J. xii.)

Height of barometer in metres	0·73	0·74	0·75	0·76	0·77	0·78	0·79
Percentage strength of residue in HCl . .	20·30	20·28	20·26	20·24	20·22	20·20	20·18

It will be seen that in cases where the barometer stands at about 0·76, the percentage of HCl may, without incurring great error, be taken as 20·24. 180·3 grms. of such an acid are accordingly equivalent to 36·5 gr. of HCl.

c. Concentrated hydrochloric acid of known specific gravity is so far diluted with water that it contains rather *more* than 36·5 gr. HCl. In a measured quantity (V c.c.) of this acid, carbonate of sodium is dissolved in the cold in the proportion of 53 milligrammes to every 1 c.c. of the acid. A few grammes of sulphate of sodium are then added, and the whole is boiled to expel the carbonic acid. The sulphate of sodium is added to prevent the evolution of hydrochloric acid.

The liquid so prepared contains, besides the neutral salts, only the excess of acid

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* Gay-Lussac's method of determining silver has recently been investigated by Mulder (see Mulder, "Die Silberprobir-methode," etc., Leipzig bei Weber). He has made the singular observation, that a mixture of exactly equivalent quantities of Ag and NaCl-solution gives precipitates wth *both* reagents. Of either of the two solutions a quantity equivalent to $\frac{1}{2000}$ of the silver just precipitated is to be added, before the formation of precipitates ceases. Stass has, in the course of his determinations of atomic weights, made a similar observation; but according to him, the limits of the state of indifferent equilibrium are narrower. These observations show that in order to attain the highest possible degree of accuracy, a strictly empirical procedure must be adopted.

† For an acid whose strength is between twenty and thirty per cent. the relation between specific gravity s, and percentage p, is given by the equation—

$$p = 200\,(s-1) + 0{\cdot}3.$$

whose quantity has to be determined in order to find the strength of our test-acid. For this purpose the mixture is coloured slightly red with solution of litmus, and an arbitrarily diluted caustic soda solution is added while the liquid is hot, till the last drop causes a decided blue colour (without mixture of violet). The quantity of soda (t c.c.) required to produce the effect is noticed.* On the other hand, a fixed volume (v) c.c. of the test-acid is measured, and in exactly the same manner, the quantity (t^1 c.c.) of caustic soda required for its neutralisation is determined.

From the last test, we have found that 1 c.c. of the arbitrarily diluted soda is equivalent to $\frac{v \text{ c.c.}}{t^1}$ of our acid. Hence we had previously added $\frac{t}{t^1} v$ c.c. more of this acid than is necessary for the neutralisation of V. 53 miligrm. of carbonate of soda, *i. e.* $\left(V - \frac{vt}{t^1}\right)$ c.c. of test acid would have exactly sufficed to neutralise the weighed quantity of carbonate of sodium. If, accordingly, we dilute $\left(V - \frac{vt}{t^1}\right)$ c.c. of acid to V c.c., then 1 c.c. of the mixture will contain exactly 1 milligramme-atom of HCl. In most cases, however, it is better not to perform this dilution, but to note that 1 c. c. test-acid contains $\left(\frac{V}{V - \frac{vt}{t^1}}\right)$ 36·5 milligrammes of HCl.

3. *Test Sulphuric acid.*—It is not necessary to have this as well as the hydrochloric test-acid. Nevertheless it has over the latter the important advantage of being wholly non-volatile when boiled in dilute solution. It can be prepared according to the method described for hydrochloric acid under (c).

4. *Test Caustic soda,* which is, volume for volume, exactly or nearly equivalent to the test-acid. Carbonate of sodium is rendered caustic in the ordinary manner, and so far concentrated that the requisite strength is nearly attained. A small quantity more of milk of lime is then added, the liquid allowed to cool (the air being excluded), and the clear liquid drawn off by a syphon. For the exact determination of its strength, 50 c.c. test-acid are poured into a porcelain basin, a few drops of litmus are added, and then the soda-solution is poured in from a burette till the colour begins to deepen. A decided reaction is recovered by addition of 1 c.c. of test-acid; about 2 grms. of sulphate of soda are then added (if hydrochloric acid is being employed); the liquid is heated to boiling, and soda is again poured in, till the liquid exhibits a distinct blue colour. The calculation of the result requires no explanation.

5. *Solution of Litmus.*—Powdered litmus is digested in the cold with twenty times its weight of water, the solution filtered, and so exactly saturated, that 1 c.c. of the litmus solution diluted with about 100 c.c. water, is turned decidedly red by $\frac{1}{20}$ c.c. of test-acid, and decidedly blue by the same quantity of test-alkali.

Acidimetry.—Free acids in aqueous solutions, if these be free from magnesia, alumina, and the heavy metals, and are not deeply coloured, may be determined in a manner which will be sufficiently clear from paragraph 4. If hot solutions are used, the caustic soda may without injury contain a little carbonic acid. But if we are compelled to work in the cold, in consequence of the presence of salts of ammonia, or because the acid to be determined cannot be prevented from evaporating by addition of sulphate of sodium, caustic soda must be employed which is almost perfectly free from carbonate. But even in such case, the termination of the reaction is not so easily recognisable as when the solution is warm. It is best detected by dropping in the soda rather quickly and without intermission, till the liquid, after stirring, remains distinctly blue for some seconds. The gradual change of this colour to violet is no evidence of the solution not being neutral. Such change depends upon the subsequent action of carbonic acid upon the litmus. In the determination of weaker acids, such as the organic, the same exactitude of reaction is not observed as occurs in the determination of sulphuric, nitric, hydrochloric, and other strong acids. It must be also noticed that many substances somewhat modify the blue colour which is the criterion of completed reaction. In presence of many substances, such as ammoniacal salts, &c., the change of colour from red to blue does not occur so quickly and decidedly as when these substances are absent; and in a few instances, as when acetic acid is present, the real point of saturation is not reached until after the change of colour has taken place. In order to render the analysis, in such cases as these, as accurate as possible, it is advisable to make a control experiment under the same conditions as occur in the real determination. Thus, for instance, if the strength of an acetic acid be required, it will not be sufficient to make an analysis in the ordinary way, because the neutral, acetates of sodium and potassium have an alkaline reaction, and this will mask the true point of saturation; it is best, therefore, to prepare a solution of acetic acid of

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* The change of colour is best seen in a porcelain basin, or in a flask standing on white paper.

known strength—by adding a known quantity of standard sulphuric acid to excess of acetate of sodium, and to determine how much standard soda-solution is necessary to bring about a definite change of colour in this acid solution. The strength of the soda-solution being thus empirically determined with acetic acid, the real analysis can be made without any reference to hypothesis.

Alkalimetry.—Caustic alkalis and their carbonates are easily determined in a manner which is so analogous to the method given (2, *c.*) for the preparation of standard acid, that a fuller description is unnecessary. If many such determinations are to be made, it is advisable to employ test-sulphuric (not hydrochloric) acid, and so to dilute the soda that it saturates the test-acid, volume for volume. If ammonia is to be determined, the reneutralisation by soda must be performed in a perfectly cold solution.

Baryta, Strontia, and Lime, and their carbonates, are determined exactly as the the fixed alkalis. But hydrochloric acid must be employed and no sulphate of sodium can be added, otherwise sulphates of these earths are precipitated, and such precipitates influence the litmus reaction. If only a small excess of acid has been used, the quantity of hydrochloric acid lost by a boiling of short duration is very inconsiderable. If this excess of acid does not occur in the first analysis, it may be made to do so in a second one (see page 117).

3. ANALYSIS BY OXIDATION AND REDUCTION.—It is known that most elements combine in various proportions with oxygen or its substituents; that lower oxides or chlorides are converted into higher oxides or chlorides, by the direct or indirect addition of oxygen or chlorine; and that these higher compounds often give up a portion of their oxygen or chlorine when in contact with reducing agents. Amongst the innumerable reactions of this kind, all those can be employed which occur quickly, and in which the termination of the reaction may be recognised with distinctness. Amongst the numerous methods of volumetric analysis of this kind hitherto proposed, we shall mention only the most important. These may be divided into two classes: (*a*) those in which permanganic acid is the oxidant,—(*b*) those in which iodine acts as oxidant.

(*a*). With PERMANGANIC ACID:

1. *Determination of Iron.*—If a solution of permanganate of potassium be added to a strongly acid and dilute solution of a protosalt of iron, the Mn^2O^4K gives up $\frac{5}{8}$ of its oxygen to the iron, converting it into sesquisalt, and is itself converted into a manganosum- and a potassium-salt of the acid added; *e. g.*:

$$2Mn^2O^4K + 10SO^4Fe^2 + 8SO^4H^2 = 2SO^4Mn^2 + SO^4K^2 + 5(SO^4)^3Fe^4 + 8H^2O.$$

The deep purple red colour of the permanganic acid is continually destroyed as long as any protoxide of iron is present; but as soon as all the protoxide of iron is converted into sesquioxide, the next drop of the reagent, even if the solution is very dilute, gives a distinct rose-red coloration. Hence it is clear that protoxide of iron may be determined by means of permanganate of potassium. A convenient standard solution is obtained by dissolving about 8 grammes of the commercial crystallised salt in 1 litre of water; 1 c.c. of such solution oxidises, according to the relative purity of the salt, from 12—14 milligrammes of iron present in the form of protoxide. On account of this uncertainty, and because the solution gradually though slowly decomposes, a fresh estimation of the strength of the solution must precede every series of iron determinations. For this purpose, 0·5 grm. of pure iron (thin harpsichord wire is almost perfectly pure) is dissolved in a great excess of pure dilute sulphuric acid, the air being as far as possible excluded. Mohr recommends the double salt, $SO^4FeNH^4 + 3H^2O$, as a standard. The air-dry salt does not oxidise in air: it contains $\frac{1}{7}$ of its weight of iron. The solution is then allowed to cool, and is diluted with water free from air to between 0·4 and 0·5 litres. Chameleon solution is added from a burette to this liquid, till the colour of the last drop no longer disappears. From the result it is easy to calculate how many milligrammes of iron are oxidised by 1 c.c. of the chameleon solution. In order now to determine the quantity of iron in a given substance, so much of the substance as will contain about 0·5 gr. of iron is dissolved, if possible, in water or sulphuric acid; hydrochloric acid should be used only when it cannot be avoided. If all the iron is dissolved as protoxide, the solution is diluted to about 0·4 or 0·5 litres, and examined just as was done in the case of the standard solution above described. If the iron is present partly or wholly as sesquioxide, this must, previous to the dilution by boiling with zinc free from iron, be completely reduced to the state of protoxide. The reduction may be considered complete when the solution has become completely or nearly colourless. If any metals such as arsenic, copper, &c. are hereby precipitated, they must be removed by quick filtration through bibulous paper.

That the determination may be accurate, it is necessary—1. That the solution be very dilute, in order that the yellow colour of the sesquioxide of iron formed may not interfere with the distinctness of the reaction. If hydrochloric acid be present, more water than usual must in general be added, because in concentrated solutions, hydrochloric acid reduces permanganic acid.

$$Mn^4O^7 + 14HCl = 7H^2O + 10Cl + 4MnCl$$

2. An excess of acid—if possible, of sulphuric acid—must be present. The object of this is not only to make the colour of the sesquioxide of iron faint, but also to prevent the oxygen of the air and the small quantity of air in the water used for the dilution, from exerting an oxidising action during the operation.

It is scarcely necessary to mention that protoxide of iron may in this manner be determined in the presence of sesquioxide. The principal advantage of this determination consists in the fact that the presence of many substances, which often greatly complicated weight-analyses, does not interfere with its simplicity and accuracy. Even the iron contained in ferrocyanides may be determined by means of permanganate of potassium.

The behaviour of permanganic acid towards protoxide of iron may serve for the indirect estimation of many substances which are capable of oxidising proto-salts of iron. It is only necessary to allow the substance to act upon a known quantity of iron in excess dissolved as protoxide, and to estimate the amount of protoxide unacted upon, in the manner just described. Free chlorine, the active chlorine in chloride of lime, the higher oxides of manganese[*], nitric acid, &c., may be determined in this way. We shall subsequently discuss other and better methods of estimating these substances, and will not therefore here enter into further particulars.

2. *Determination of Copper.*—The solution of the substance in water or nitric acid is mixed with a quantity of tartrate of potassium and sodium sufficient to prevent precipitation by the subsequent addition of an excess of caustic potash. The alkaline liquid is heated to boiling, and milk-sugar is added, till all the copper is precipitated as suboxide. This is collected on a filter, washed with hot water, and digested, together with the filter, in strong hydrochloric acid and chloride of sodium. The resulting solution of $NaCl + Cu^2Cl$, is to be diluted and treated with permanganate of potassium, as in the determination of iron. The filter, if the operation be quickly performed, has no action upon the permanganic acid. Since in this reaction, 4 atoms of copper take up one atom of oxygen from the permanganic acid, every volume of our solution will oxidise as many atoms of copper (31·7 grms.), as it does of iron (28 grms).

$$5Cu^4O + Mn^4O^7 = 10Cu^2O + 2Mn^2O$$
$$\text{and} \quad 10Fe^2O + Mn^4O^7 = 5Fe^4O^3 + 2Mn^2O.$$

3. *Determination of Oxalic acid.*—When oxalic acid and permanganic acid are brought together in acid solutions, the former is oxidised to carbonic acid, the latter reduced to protoxide of manganese, which unites with the acid present:

$$Mn^4O^7 + 5C^2H^2O^4 + 2SO^4H^2 = 10CO^2 + 2SO^4Mn^2 + 7H^2O.$$

Hence oxalic acid may be determined by means of permanganate of potassium in a dilute solution containing an excess of free sulphuric acid, in a manner exactly similar to that described under iron. For the determination of the permanganic acid, either pure, air-dried, crystallised oxalic acid, $C^2H^2O^4 + 2H^2O$, or pure iron, is employed. A volume of test-solution which oxidises x atoms (x . 28) of iron, will convert $\frac{x}{4}$ atoms of oxalic acid (x : 31·5) into carbonic acid and water.

The behaviour of permanganic acid towards oxalic acid may be employed for the valuation of commercial peroxide of manganese: 1 grm. of the *very finely* powdered peroxide is mixed with a weighed quantity (about 1·5 gramme) of crystallised oxalic acid and a considerable excess of pure dilute sulphuric acid, and warmed till the peroxide of manganese is decomposed. Water is added, the solution allowed to cool, and the excess of oxalic acid determined as above: 1 atom of peroxide of manganese transforms 1 atom of oxalic acid into carbonic acid:

$$Mn^2O^2 + C^2H^2O^4 + SO^4H^2 = SO^4Mn^2 + 2CO^2 + 2H^2O.$$

(*b*). METHODS IN WHICH IODINE ACTS AS OXIDISING AGENT.—Iodine in aqueous solution, in presence of oxidable substances, often acts upon the elements of water so as to form hydriodic acid with its hydrogen, while the oxygen acts upon the substance present. Now as the smallest quantity of free iodine may be recognised by its property of blueing starch-solution, whereas hydriodic acid and the iodides are without action upon starch, the substances mentioned may often be determined by mixing their

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[*] The determination of nitric acid becomes exact only when the reaction takes place in an atmosphere of hydrogen, but this precaution being taken, N^2O^5 oxidises exactly 12Fe. (Fresenius.)

aqueous solutions with starch-solution, and then adding a standard solution of iodine in iodide of potassium, until permanent blue coloration occurs. In order that this reaction may succeed, the substance to be oxidised must, even in very dilute solution, possess the property of decolorising the iodide of starch which has been locally formed. For examples of determinations of this kind, we will take the following.

Hyposulphurous acid, as potassium-, or sodium-salt, in neutral or alkaline solutions (made alkaline by bicarbonates of the alkalis), acts upon iodine in such a manner that tetrathionates of alkalis and metallic iodides are produced, *e.g.*:

$$2S^2O^3Na^2 + 2I = 2NaI + S^4O^6Na^2.$$

Arsenious acid, in the form of an alkali-salt, is converted by iodine into arsenic acid, in a solution made distinctly alkaline by carbonate or bicarbonate of an alkali-metal. Iodine must be added till the iodide of starch formed is no longer decolorised on the addition of bicarbonate of sodium; 4 atoms of iodine (508 pts.) oxidise 1 atom of arsenious acid (198 pts.):

$$As^2O^3 + 4I + 2H^2O = 4HI + As^2O^5.$$

Sulphurous acid, may be determined like hyposulphurous acid in solutions rendered feebly alkaline by an alkaline carbonate. The product formed is sulphuric acid:

$$SO^2 + 2I + 2H^2O = 2HI + SO^4H^2.$$

If we endeavour to determine *free* sulphurous acid by iodine, very divergent results are obtained when the solution is strong. In such cases, the quantity of sulphurous acid converted into sulphuric acid varies very much, according to the quantity of water present and the rapidity with which the iodine is added. If, however, before adding the iodine, the solution is so far diluted with water free from air, that less than 0·4 grm. of sulphurous acid is contained in 1 litre of water, the reaction, $2I + 2H^2O + SO^2 = 2HI + SO^4H^2$, occurs with perfect regularity.

The circumstances under which this reaction takes place, were determined by Bunsen (Ann. Ch. Pharm. lxxxvi. 265), and applied to a series of very accurate volumetric determinations, the most important of which we shall here explain.

Analyses by means of Iodine and Sulphurous Acid.

Reagents.—1. Pure iodide of potassium. 2. Pure hydrochloric acid. 3. Freshly prepared, thin, very clear starch-solution.* A dilute solution of iodide of potassium, mixed with starch and hydrochloric acid, must give a mixture which remains colourless for several minutes.

4. A standard solution of iodine in iodide of potassium, 5 grms. of commercial iodine, and 10 to 12 grms. of iodide of potassium, are dissolved in about 20 c.c. water, and as soon as all the iodine is dissolved the solution is diluted to 1 litre.

5. A solution of sulphurous acid in distilled water. This must be so diluted that about 10 volumes of it are necessary to decolorise 1 volume of the iodine-solution (4). This solution should be prepared in quantities of 10 to 20 litres, and allowed to stand about an hour excluded from the air, before use, so that the oxygen contained in the dissolved air may be absorbed by the sulphurous acid. It may be advantageously kept in an earthenware vessel, provided with a tap at the bottom, and a fine drawn out tube above to allow the air to enter. The strength of such a solution may be considered as constant during the performance of one analysis.

The first question is to determine *exactly* the strength of the iodine-solution, already approximately known. If we had a small quantity of perfectly pure iodine of known weight, this might be easily done by comparing such iodine with the standard-solution by means of the same sulphurous acid. Such a quantity of iodine to serve as a measure, is obtained by boiling between 200 and 400 milligrammes (= *A*) of pure anhydrous bichromate of potassium with fuming hydrochloric acid, and collecting the evolved chlorine in a solution of iodide of potassium (for one part of the bichromate about 20 parts iodide of potassium are employed). 1 atom (294·8) of bichromate liberates under these circumstances 6 atoms of iodine (6 × 127·0):

$$Cr^4K^2O^7 + 14HCl = 7H^2O + 2KCl + 2Cr^2Cl^3 + 6Cl$$
$$6Cl + 6KI = 6KCl + 6I$$

In order to perform this operation without loss, the following method is adopted.

On a glass tube of about 4—5 mm. internal diameter, a bulb of about 30 c.c. capacity is blown, and a flask is thus obtained of the form shown in *fig.* 48. To a short piece of the same tubing, a longer and narrower tube is fused, drawn out at *d*, and bent as shown in the figure. If the neck of the flask and the adapter-tube be ground flat and connected with caoutchouc, in such a manner as to bring them close together, an appa-

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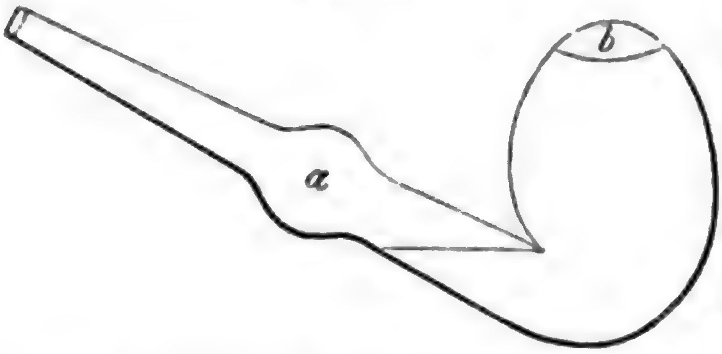
* Starch-solution, when filtered and saturated with chloride of sodium, may be kept a long time without decomposition. (Mohr.)

ratus is obtained for the evolution of chlorine, which is scarcely inferior to one consisting wholly of glass. The caoutchouc tube before use must be freed from adhering sulphur by boiling with very dilute caustic soda and thorough washing with water.

A retort of about 150 c.c. capacity (*fig.* 49) serves to hold the solution of iodide of potassium. The neck of the retort is widened at *a*, to receive any solution driven back by the expelled air. In order to make the determination, we bring the bichromate of potassium into the flask, which is then filled to $\frac{2}{3}$ with fuming hydrochloric acid; the delivery-tube is attached, and placed so far in the retort (filled up to the commencement of the neck with iodide of potassium solution), that the chlorine which is not immediately absorbed must collect at *b*. The flask is first gently heated till the decomposition is complete, then more strongly, in order to drive over every trace of chlorine into the iodide of potassium solution by means of the gaseous water and hydrochloric acid. The retrogression of the iodide can scarcely take place if some care is taken, because it can only occur very slowly, in consequence of the small volume of the apparatus and the fineness of the point *d*. After the hydrochloric acid vapours have been evolved for about five minutes, it may be assumed that all the chlorine is expelled. Without discontinuing the boiling, the delivery-tube is withdrawn from the retort, and the vapours are conducted into some fresh solution of iodide of potassium, the boiling being continued for a few moments longer. If this solution remains uncoloured, the operation may be regarded as successful.

Fig. 48.

Fig. 49.



The contents of the retort (coloured deep brown by iodine) are quickly cooled, and poured out into a beaker glass, and portions of 400 to 450 c.c. of the dilute sulphurous acid are successively added, without loss of time, until the liquid is colourless. The measurement of the sulphurous acid is effected in a flask which contains, up to a mark on its narrow neck, from 400 to 450 c.c., but whose capacity need not be accurately known. The flask is rinsed out with the sulphurous acid, filled up to the mark, and emptied in a definite manner, which should be strictly adhered to during the same analysis. Direct experiments have shown that the volume of the liquid delivered is sufficiently constant.

The liquid decolorised by sulphurous acid contains an excess of this body. Starch and then normal iodine-solution are therefore added till blue coloration occurs. Let the volume of the latter necessary for this be t^1 c.c. Immediately afterwards, one of the measures of sulphurous acid previously employed is taken, and the volume (t c.c.) of standard iodine-solution determined which is necessary for its oxidation. If, then, the number n of the flasks of sulphurous acid which were added to the iodide of potassium solution from the retort has been noted, the strength of the normal solution may be easily calculated.

Let us call, for brevity, the contents of the flask the "volume." From the result of the determination just given, we find that nt c.c. normal iodine-solution were necessary for the oxidation of n volumes sulphurous acid. For such oxidation, t^1 c.c. of the same iodine-solution, together with the quantity of iodine produced by the distillation of A milligrammes of bichromate of potassium with hydrochloric acid, were also sufficient. This amount of iodine $\left(A.\ \frac{3 \times 127}{147 \cdot 4}\right)$ millg. is therefore equivalent to $(nt - t^1)$ c.c. of iodine solution. Hence 1 c.c. of the latter contains

$$\frac{A \times 3 \times 127}{147 \cdot 4\ (nt - t^1)} \text{ milligrammes of free iodine, or}$$

$$\frac{A \times 3}{147 \cdot 4\ (nt - t^1)} = T \text{ milligramme-atoms of free iodine.}$$

Inasmuch as all subsequent analyses depend upon these determinations, the latter must be performed two or three times, and the mean taken of the results (which should nearly agree). The most various analyses may be performed by means of an exactly determined iodine-solution. We will take the following examples.

1. The determination of *sulphurous*, *hyposulphurous*, and *arsenious* acids has been already described.

2. *Sulphuretted hydrogen* may be determined similarly to sulphurous acid, in a solution containing less than 0·4 grm. in 1 litre; but from some unexplained cause the results are only approximately exact. The reaction which here occurs is represented by the equation: $H^2S + 2I = 2HI + S$.

3. Determination of free *Iodine*, *Bromine*, and *Chlorine*. Iodine dissolves directly in a solution of iodide of potassium; bromine and chlorine form bromides and chlorides, liberating an equivalent of iodine. The quantity of the latter is determined by adding excess of sulphurous acid (n volumes), then starch, and finally solution of iodine (t^1 c.c.), until the well-known reaction occurs. If now t c.c. of iodine solution were necessary for the oxidation of 1 volume of sulphurous acid, the liberated iodine must be equivalent to $nt - t^1$ of iodine-solution, or the chlorine, bromine, or iodine must have the value of $(nt - t^1)T$ milligramme-atoms.

4. Determination of the *Oxides of Chlorine which contain less than five atoms of Oxygen for two atoms of Chlorine.* All these substances are decomposed by iodide of potassium and hydrochloric acid in the following way:

$$Cl^2O^x + 2xHCl = xH^2O + 2(x + 1)Cl.$$

The free iodine is determined according to (3). Commercial bleaching powders are tested for the amount of active chlorine which they contain, by treating them with an excess of iodide of potassium and enough hydrochloric acid to cause a slightly acid reaction. Each atom of active chlorine liberates an atom of iodine:

$$CaClO + CaCl + 2HCl + 2KI = 2CaCl + H^2O + 2KCl + 2I.$$

5. *Chlorates.*—According to Bunsen's experiments, these salts when distilled with hydrochloric acid do not give up free oxygen, but only free chlorine and lower oxides of chlorine. If the products of distillation be received in excess of iodide of potassium, the final result is the liberation of 6I for ClO^3H. Such iodine may be determined according to (3).*

6. *Iodates.*—One atom of free iodic acid decomposes with 5 atoms of hydriodic acid to 3 atoms of water and 6 atoms of free iodine ($HIO^3 + 5HI = 6I + 3H^2O$). This reaction may serve for the determination of iodic acid. On the other hand, pure iodate of potassium may be conveniently employed for determining the strength of the normal iodine-solution. (Bunsen.)

7. *Metallic oxides* containing a portion of their oxygen in such a state that it liberates an equivalent quantity of chlorine on boiling with strong hydrochloric acid, may be determined by boiling them with fuming hydrochloric acid, collecting the chlorine in iodide of potassium, and determining the iodine set free according to (3). To this class belong all peroxides, the higher oxides of manganese, chromic acid, and other metallic acids, &c. &c. In analysing manganic oxides, a weak hydrochloric acid of about 20 *per cent.* must (exceptionally) be employed, because on using fuming hydrochloric acid, chlorine is apt to escape. The calculation scarcely needs any explanation. The amount of free chlorine, if we retain the usual symbols, amounts to $(nt - t^1)T$ milligramme-atoms. Half this number of atoms of active oxygen are therefore present, and these stand in a known simple numerical relation to the number of atoms of the substance to be determined.

8. *Metallic oxides* which may be peroxidised by chlorine, are determined by boiling them with a weighed *excess* of bichromate of potassium and hydrochloric acid, receiving the excess of chlorine in iodide of potassium solution, and determining it according to (3). As an example of the calculation, let us take the determination of protoxide of iron. Let the amount of bichromate of potassium employed be A milligrammes; this ($\frac{A}{147{\cdot}4}$ milligramme-atoms), if iron had been absent, would have liberated $\frac{3\,.\,A}{147{\cdot}4}$ milligramme-atoms of free iodine. If instead of this, we actually find only $(nt - t^1)\,T$ milligramme-atoms, then:

$$\frac{3\,.\,A}{147{\cdot}4} - (nt - t^1)\,T$$

milligramme-atoms of chlorine must have served for the oxidation of the iron. Or:

$$\left\{\frac{3\,.\,A}{147{\cdot}4} - (nt - t^1)T\right\}.\ 2 \times 28$$

milligrammes of iron must have been present.

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* If perchloric acid were produced in this reaction (and its *entire* absence has not yet been proved), the method, as applied to chlorates, would not give accurate results. Bunsen, in his Memoir, gives only one determination of chlorate of potassium, which, however, agrees very well with theory.

Having become acquainted with the most important volumetric methods we may now consider a point in connection with the calculation of the results. If a long series of determinations of the same kind have to be performed successively, the time necessary for their calculation is of great consequence, and it is important to consider the best way of simplifying it as much as possible. This may generally be effected by so choosing arbitrary magnitudes which occur in the calculation, as the weight of the substance, the strength of the normal solution, &c., that the mathematical expression for the result may be as simple as possible. The following examples will illustrate this:

1. A number of soda determinations have to be made with an acid which contains 1·017 milligramme-atoms of sulphuric acid ($SO^4H^2 = 98$) in 1 c.c. If a milligrammes of soda be employed in the analysis, and if the volume of the acid used in neutralisation be k c.c. then the soda contains $\frac{k \times 1{\cdot}017 \times 62 \times 100}{a}$ *per cent.* of anhydrous soda (Na^2O). If now 1·017 × 62 × 100 milligrammes of soda be weighed each time, then the fraction $\frac{1{\cdot}017 \times 62 \times 100}{a}$ is $= 1$, and the percentage of the soda in caustic soda is $= k$, that is, simply equal to the number of c.c. of the standard acid used.

2. In the previous division (8), we have considered the determination of iron by means of iodine-solution and sulphurous acid. If ϵ milligramme of the iron compound be employed for the analysis, the percentage (x) of iron is derived from the formula

$$x = \frac{2 \times 28 \times 100 \left\{\frac{3\,A}{147{\cdot}4} - (nt - t^1)T\right\}}{\epsilon}$$

in which the letters have the signification before given. It is clear that the calculation is considerably simplified if (1) T be a round fractional number, for instance, $\frac{1}{10}$, (2) if A be made a simple multiple of 147·4, for instance, 5 × 147·4 milligrammes. (3). By taking ϵ so as to be a simple submultiple of 2 × 28 × 100, for instance, 30 × 28 milligrammes.—W. D.

ANALYSIS (VOLUMETRIC) of GASES. This branch of analysis has of late attracted much attention from chemists; but the chief improvements and developments relating to it are due to Professor Bunsen. Previous to his researches on the subject, the processes adopted for measuring and analysing gases were so exceedingly imperfect, the inaccuracies introduced so numerous, and even the reagents made use of so defective, that only the most variable results could be obtained; now, on the contrary, gases may be analysed with an accuracy which cannot be equalled in any other branch of chemistry. So far indeed as accuracy and simplicity of manipulation are concerned, Bunsen's method leaves little to be desired; but it is long and tedious, even a simple analysis requiring some days for completion. The necessary calculations for the reduction and correction of the observations are also numerous and require considerable time and attention.[*] To obviate these inconveniences, several methods have of late been proposed, by which the composition of a gas may be accurately determined in a very much shorter time, and without the calculations formerly necessary.

The arrangement of the subject adopted in this article is: first a description of the apparatus and general method proposed by Bunsen; then that of the more recent and expeditious methods; and lastly, the processes, which to a certain extent are common to all the methods, for separating and estimating the different gases.

According to the method of Professor Bunsen, the gases are collected and measured in graduated tubes over mercury. For this purpose, two straight glass tubes are used; one of them, which should be about 250 mm. long and 20 mm. in diameter, is termed the absorption-tube, and the other which is from 500 to 600 mm. long, and 20 mm. in diameter, is termed the eudiometer (*figs.* 50, 51). The absorption-tube is provided with a sort of lip as shown in the figure, to enable the operator to pass the gas easily out of this tube into the eudiometer. As this latter tube is the one in which the combustible gases are exploded, two platinum wires must be fused into the closed end of it, for the passage of the electric spark. This is done by strongly heating the end of the tube in the blowpipe lamp, and then just touching it at the point where the wire is to be introduced, with a hot platinum wire; to this the glass strongly adheres, and by this means is drawn out to a fine thread, which, on being cut off close to the eudiometer, is found to be hollow; through this hole a platinum wire is introduced, and the glass carefully fused all round it. A second platinum wire is then by similar means fused into the opposite side of the eudiometer. These wires should not project straight across the tube, as they are then apt to become bent and moved from their proper distance

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[*] For a more detailed account of Bunsen's method of analysis, and for further information on gasometry in general, we would refer the reader to Bunsen's "Gasometry," translated by Roscoe. (Walton and Maberly.)

apart on filling the tube with mercury;—if straight, they would also prevent the eudiometer from being properly cleaned: it is consequently most convenient to have them bent so as to lie against the rounded top of the eudiometer. The ends of the wires should be at the distance apart of about 1 to 2 m.m. In order to ascertain whether the wires have been properly fused in, so that the contact of the platinum and glass may be perfect and no probability of leakage can occur, the eudiometer is filled and inverted in a mercury trough, and then, while held in a vertical position, sharply rapped against the bottom of the trough; this communicates a movement to the mercury in the tube, which sinking for a moment leaves a vacuum at the top, whereupon if the wires are not fused in absolutely air-tight, a row of small bubbles will be seen rising from the defective point.

Fig. 50.

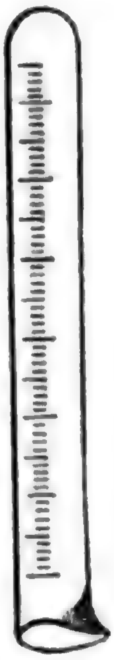
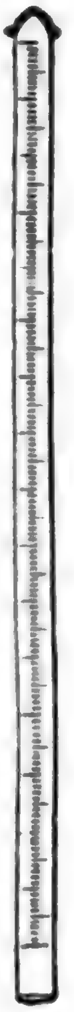


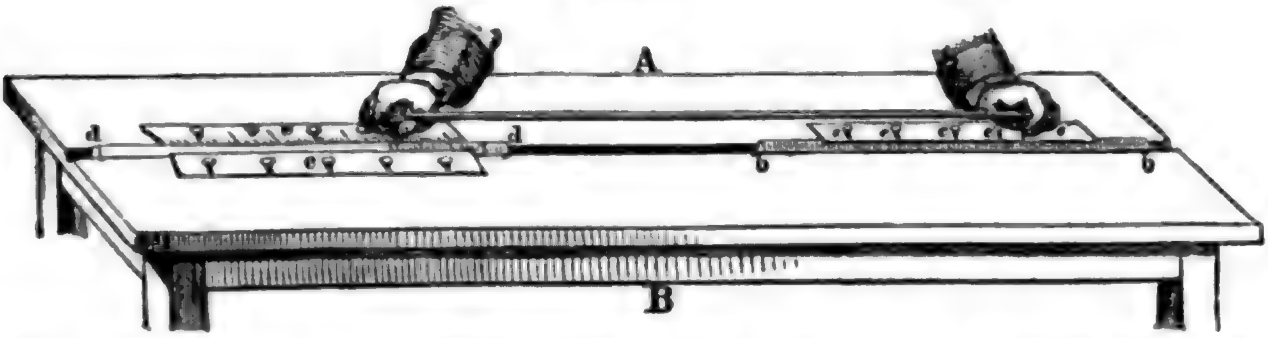
Fig. 51.



Having proved the tube to be air-tight, the next operation is to etch, by means of hydrofluoric acid, a millimetre scale on it and on the absorption-tube. This may easily be done by the following process, which was also suggested by Professor Bunsen. The tube to be etched is heated up to the temperature at which bees-wax melts over a fire, being held by means of a stick which passes through a cork fitted into the open end of it. The tube is then covered as uniformly as possible with melted wax, which is best done by painting it all over with wax, by means of a brush or feather. During the cooling, it should be continually turned round in the hand, so as to keep the wax equally distributed over the whole surface. If the tube when cold is found to be completely covered with wax, it is then ready for etching.

Fig. 52 represents the apparatus used for this purpose, A B is a table or large board, with a groove running along it of such size that the tube to be graduated will lie easily in it; *d d* represents this tube, which is firmly held in its place by two brass plates *e e*, screwed down upon it. At the other end of the groove, a standard tube *b b*, is also firmly fixed by means of a brass plate, and on this tube is the scale which is to be exactly copied on the wax covering the tube *d d*. This is done by means of a long bar of wood, to one end of which is fixed a steel point, and to the other a kind of knife. The rod is held by the ends as shown in the figure, the right hand guiding the knife. In using the apparatus, the steel point is allowed to fall into one of the divisions on the standard tube, which are purposely deeply etched, and while it is held there, a cut is made by means of the knife on the wax covering the tube. The length of this cut, and the consequent breadth of the scale, is regulated by the distance between the two brass plates *e e*. As soon as this first stroke has been made, the wooden rod is gently moved a little forwards until the point falls into the next mark on the standard tube; then a second cut is made in the wax, and so on. The steel point should always rest against the brass plate *e e*, which will then serve to keep it in the same straight line. In order to render the reading of the scale more easy, it is convenient to have every fifth stroke on it longer than the others; which is easily accomplished by having slits made in the brass plate *e*, at the distance of 5 mm. apart, so that when the knife arrives at one of these slits, it passes further across the tube than in other cases. Before removing the waxed tube, it must be carefully examined, and if any false strokes are seen, they may be removed by applying a thin heated wire to the spot: then, when the wax has cooled, a fresh stroke may be made. The tube is now removed, and at each centimetre, the figures indicating the number of millimetres from the top are scratched in the wax by means of a needle. If any of the wax has been removed from the tube by the pressure of the brass plates, these places must be carefully re-covered, and the tube is then ready to be exposed to the hydrofluoric acid.

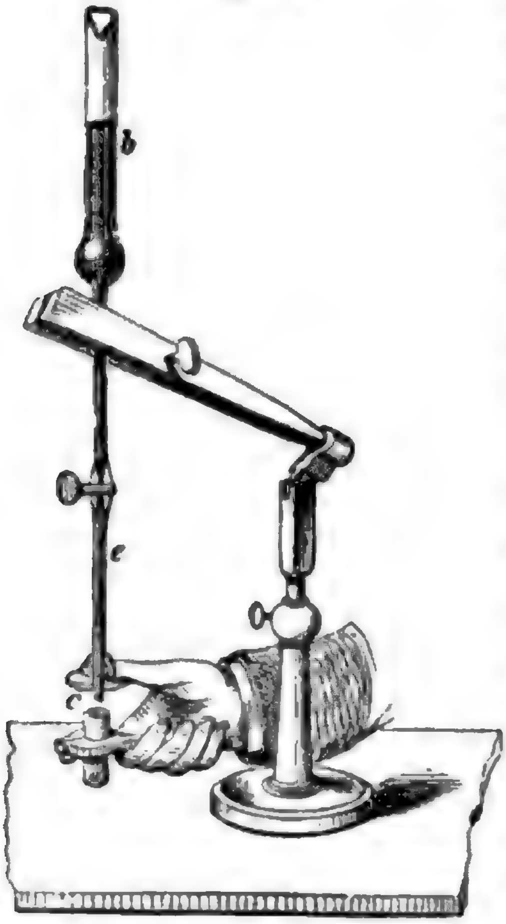
Fig. 52.



This is most conveniently done in a kind of long narrow leaden dish. Powdered fluor-spar is strewed along the bottom, and a large excess of sulphuric acid added; heat may then be applied. As soon as the gas comes off abundantly, the lamp is removed, the tube laid over the dish resting on two wire supports, and the whole is covered with a sheet of paper. When the tube has remained there about three minutes it should be removed and one of the divisions examined by passing the nail over it, to ascertain to what extent the etching has taken place. In from three to six minutes, most tubes will be sufficiently acted on. The etching may also be accomplished without applying heat to the hydrofluoric mixture; in this case the tube must be left in contact with the acid for several hours. This latter method yields perhaps the most distinct graduation. In order to render the scale still more clear, it should be rubbed over with a mixture of vermilion and copal varnish, which fills and hardens in each of the divisions, rendering them very evident to the eye.

Since no tube is of precisely the same diameter for any length together, the scale thus etched bears evidently no constant relation to the cubic capacity of the tube. In order then to ascertain to what extent the capacity varies in different parts of tube equal volumes of mercury must be poured into it, and the space they occupy read off on the scale. *Fig.* 53 represents a convenient form of apparatus for always obtaining, these equal volumes of mercury. *a* is a small glass tube fixed in a handle and capable of containing about that amount of mercury which is required to fill the eudiometer through 20 mm. of its length. *c* is a glass plate, on the top of which the two ends of a strip of caoutchouc are fastened by sealing wax, so as to form a loop which is slipped over the thumb. By turning the stopcock, which allows the mercury to flow from the reservoir *b*, the glass measure, the top of which must be ground perfectly even, is completely filled, and the mercury rises in a curve above the top; on depressing the plate *c*, the excess is expelled and the tube obtained perfectly full: care must, however, be taken that no bubbles of air remain adhering to the sides. In filling the measure, it is well to allow the end of the tube *e* to rest on the bottom of it, and only gradually to withdraw it when nearly full of mercury. The tube to be calibrated is firmly held in a perpendicular position by means of a clamp, and the measures of mercury are then carefully poured in, any bubbles of air which may remain adhering to the tube, being removed by means of a small stick or piece of whalebone. After each addition of mercury, the height which it occupies on the scale is read off. In order to prevent errors from parallax, this should be done by means of a telescope fastened to a clamp which moves on a perpendicular support. In all readings-off, it is the position of the highest part of the mercury meniscus on the scale that is observed. This process for determining the cubic capacity of the tube should always be gone through twice, and the mean of the two series of observation taken as the basis of calculation. An example will best show how these calculations are made and the results tabulated. The height of the mercury in the tube after the successive additions of the measured quantity is,

Fig. 53.



	diff.
9·1	
23·0	13·9
36·6	13·6
50·15	13·55

In the second column is expressed the height which this constant quantity of mercury occupied. This varies of course with the capacity of the tube, increasing as the tube diminishes, and diminishing as the tube increases in size. One of these differences, generally the largest, is taken as the standard, say 13·9, that is, 13·9 volumes of mercury have been found to occupy on the scale:

mm.
1 × 13·9 — 9·1
2 × 13·9 — 23·0
3 × 13·9 — 36·6
4 × 13·9 — 50·15

This gives the relative values of the scale at these particular points, and it only remains to interpolate the respective values of each division between these successive points. In the first instance, between 9·1 and 23·0, each millimetre will represent exactly 1 volume of mercury; but in the second instance, where the 13·9 vols. of mercury occupy only a length of 13·6 mm. where the tube in fact is broader, each division will have a value equal to $\frac{13\cdot9}{13\cdot6} = 1\cdot022$, and this number represents the capacity of each millimetre between 23·0 and 36·6. Again the capacity of each division between 36·6 and 50·15 is $\frac{13\cdot9}{13\cdot55} = 1\cdot025$. In this way is formed a table, which, although perfectly arbitrary, is relatively correct, the amount of error arising from the alteration of the size of the tube between each reading-off of the height of the mercury, being quite inappreciable, when the measured quantity does not extend over more than about 20 mm. The following table is calculated from the foregoing observations. In the first column, the divisions on the scale are given, in the second their arbitrary value.

9	13·80	24	28·82	39	44·17
10	14·80	25	29·84	40	45·20
11	15·80	26	30·86	41	46·23
12	16·80	27	31·88	42	47·25
13	17·80	28	32·91	43	48·28
14	18·80	29	33·93	44	49·30
15	19·80	30	34·95	45	50·33
16	20·80	31	35·97	46	51·36
17	21·80	32	36·99	47	52·38
18	22·80	33	38·02	48	53·41
19	23·80	34	39·04	49	54·43
20	24·80	35	40·06	50	55·45
21	25·80	36	41·10	51	
22	26·80	37	42·12	52	
23	27·80	38	43·15	53	

As it is always the highest point of the meniscus of the mercury that is read off on the scale, both in calibrating the tube and afterwards in measuring the amount of gas it may contain, a slight correction must be applied to every observation to correct the error which would otherwise arise from the convexity of the mercury. By referring to *fig.* 54, it will easily be seen how this error arises. (1) In calibrating the tube: if *a o a'* represent the meniscus, it is the number on the scale coinciding with the line *c c'*, that is read off, although the tube is not full up to that point by the space *a c c' a'*; and (2), in analysing a gas, when the tube is in the reverse position, the same number on the scale would be read off, although the meniscus of the mercury only coincided with the curve *n o n'*, leaving in fact a space as much below *c c'* unoccupied by mercury in this instance, as was left above it in the former one. Hence after referring to the table to ascertain the relative value of any reading-off, there must be added to it a quantity equal to the whole space *a n a' n'*. What this number is, which has always to be added can easily be ascertained by the following process. The eudiometer being fixed in a perpendicular position with its closed end downwards, a small quantity of mercury is poured into the tube, and its height carefully noted; a few drops of a dilute solution of corrosive sublimate are now added, the effect of which is entirely to destroy the meniscus, and render the surface of the mercury perfectly flat: the height $x\,x'$ at which it now stands in the tube is read off. Twice the difference of these two readings is then the quantity to be added to each observation after referring to the table of capacities.

Fig. 54.

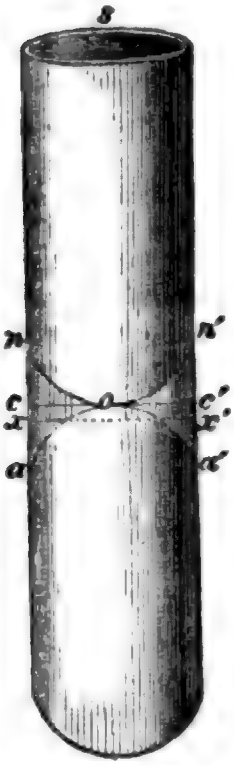
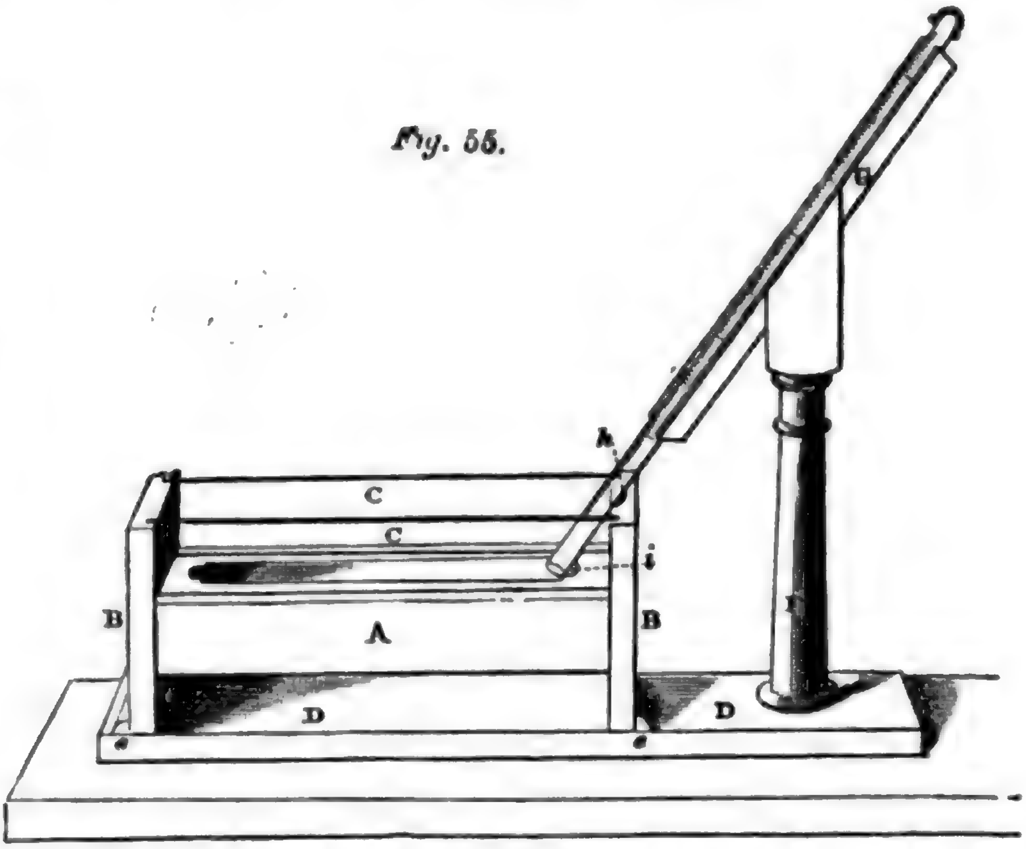


Fig. 55.



The most convenient form of mercury-trough is that proposed by Bunsen, and represented in *fig.* 55. It is about 350 mm. long, and 80 mm. broad. The two sides C C, are made of thick glass plates, and the lower part of it A, is formed out of a single piece of wood hollowed out. In order to economise the amount of mercury necessary, the inside of the trough is made round at the bottom instead of being square. G forms a convenient support for the eudiometer. Before using the trough, it should be well rubbed with corrosive sublimate and mercury, or else small bubbles of air are apt to remain adhering to the wood, and may afterwards rise into the eudiometer.

Fig. 56.

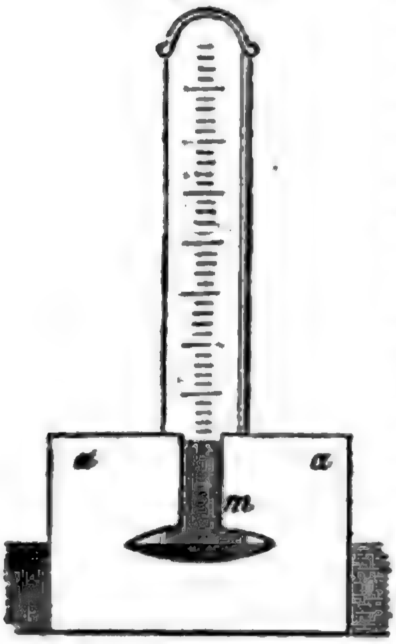
A good thermometer and barometer are of course indispensable. The length of the degrees on the thermometer scale should be such that the position of the mercury, to a tenth of a degree centigrade, may be easily read off by means of the telescope. The barometer generally used is of the syphon form (*fig.* 56). The scale is etched on the glass and the closed end is bent as shown in the figure, so that the scale on the two limbs is in the same straight line. The thermometer *t*, is placed in the open end of the barometer, and held in its place by a small piece of whalebone, which acts as a spring. Before reading off the height of the barometer and thermometer, the latter should be gently moved a little up and down, thus communicating to the mercury in the barometer a slight movement, which overcomes any adhesion between the mercury and the glass.

The kind of room which is used as a gas-laboratory when this process is adopted, is a point of very considerable importance. It should have a northerly aspect, and the walls should be thick; in fact, the room must be protected in every way from sudden changes of temperature. The mercury trough and barometer should stand on a table immediately in front of a window, if possible a double one. The table is provided with a rim round it, in order to prevent the loss of any mercury that may happen to be spilt upon it. Between every two operations in the analysis, at least half an hour must be allowed to elapse, in order that all parts of the apparatus may return to the temperature of the room. Great care must be taken in filling the eudiometer and absorption-tube with mercury, that no air remains adhering to the sides of the tube. This is most easily avoided by introducing the mercury through a funnel, to which is attached a narrow glass tube reaching very nearly to the top of the eudiometer; the mercury then rises gradually, the funnel being kept full, and expels the air very thoroughly from the tube. A small bubble of air will however generally be found to remain in contact with the platinum wires in the eudiometer; this must be got rid of by placing the thumb over the open end of the tube, and holding it in an inclined position; then, by means of a sudden jerk, the bubble may be detached from the wires, and by merely inverting the eudiometer, allowed to escape.

All the readings-off, as before stated, are made with the help of a telescope, which should be at a distance of seven or eight feet from the tubes. Care should always be taken that the division to be read off is nearly in the middle of the field of the telescope, or a slight error may arise from parallax. It is therefore convenient to have the telescope provided with a cross wire.

At each stage of the analysis, four observations have to be made: 1st, the height of the mercury in the gas-tube; 2nd, the height of the mercury in the trough as measured on the scale of the gas-tube; 3rd, the temperature; and 4th, the atmospheric pressure. The barometer and thermometer are always read off last; for before doing this, it is necessary to approach the table in order to move the thermometer, as before described, and the heat given out from the body would increase the volume of gas in the tube. In order to read off accurately the level of the mercury in the trough, it is necessary so to place a piece of white paper between the glass side of the trough and the tube, that it may reflect the light from the window on to the scale. *Fig.* 57 shows how this is conveniently arranged, the scale being seen through the slit *m*.

Fig. 57.



After each operation in the analysis, before leaving the tubes to cool, a rapid observation should be made with the telescope, in order to see that the scale on the eudiometer is in its right position, passing apparently exactly through the highest point of the meniscus, and also that the height of the mercury both in and outside the tube can be easily read off.

In order to render the observations thus made at different temperatures and pressures comparable, they must be reduced to a common standard, the one generally employed being dry air at 0° C., and under a pressure of 1 metre of mercury. If v represent the volume of gas as taken from the table, m the error of the meniscus, b the height of the mercury in the gas-tube above that in the trough, $t°$ the temperature, and B the height of the barometer, the following formula will give the corrected volume V', under the standard temperature and pressure: $\dfrac{(V + m)(B - b)}{(1 + 0{\cdot}00366t°)} = V'$.

There is also another point which must not be overlooked in the calculation, viz. the effect of the tension of water-vapour. If the gas is saturated with moisture, and the temperature at which the observation of its volume was made is known, it is then only necessary to refer to the table of tensions of aqueous vapour and extract the number corresponding to that temperature: this must be deducted from the height of the barometer. Thus, the formula for the reduction of gases saturated with aqueous vapour is $\dfrac{(V + m)(B - b - T)}{1 + 0{\cdot}00366t°} = V'$, where T is the tension of aqueous vapour for the temperature $t°$. To ensure a gas being completely saturated with moisture, a drop of water is always introduced into the eudiometer before filling it with mercury.

In order to show more clearly how these calculations are made, the following example taken from Bunsen's Gasometry, is cited, of the measurement of the same quantity of air, first saturated with moisture and afterwards dry.

		Moist.	Dry.
Observation at the lower level of the mercury . .		565·9 mm.	565·9 mm.
Observation at the upper level in the eudiometer .		317·3	310·7
Height of the column b to be subtracted from barometer		248·6	255·2
The divisions 317·3 and 310·7 correspond to the volumes in the table of capacity . . .	V .	292·7	286·0
Correction for the meniscus	m	0·4	0·4
Temperature of the air	t	20·2 C.	20·2 C.
Height of the barometer	B	0·7469 m.	0·7474 m.
Tension of aqueous vapour for 20·2 C. . .	T	0·0176 m.	

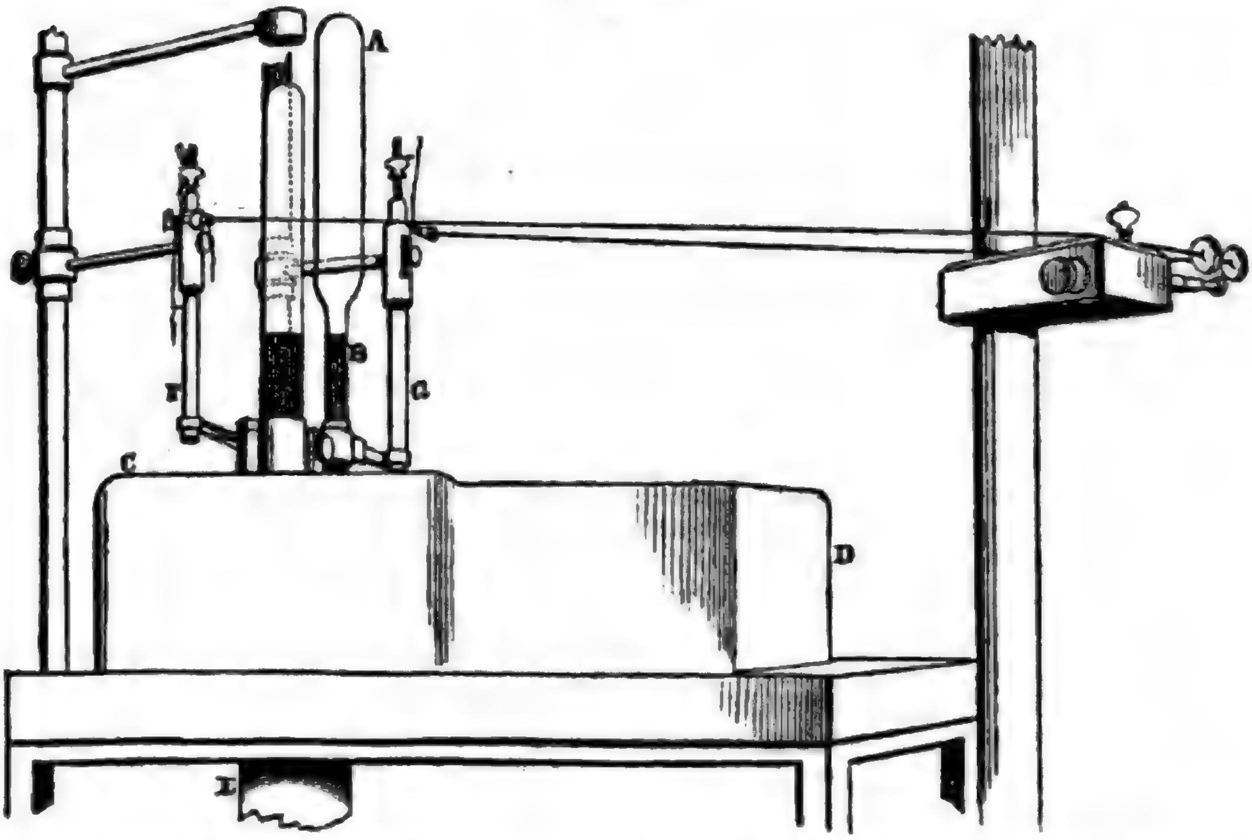
$$\begin{array}{rll}
\log.(V + m) = \log.\ 293{\cdot}1 & = & 2{\cdot}46702 \\
+ \log.(B - b - T) = \log.\ {\cdot}4807 & = & 0{\cdot}68187 - 1 \\
+ \text{compl.} \log.(1 + 0{\cdot}00366t) = \text{compl.} \log.\ 1{\cdot}0739 & = & \underline{0{\cdot}96903 - 1} \\
\log.\ V' & & 2{\cdot}11792 \\
V' & & 131{\cdot}20.
\end{array}$$

For the dry air we have:

$$\begin{array}{rll}
\log.(V + m) = \log.\ 286{\cdot}4 & = & 2{\cdot}45697 \\
+ \log.(B - b) = \log.\ 0{\cdot}4922 & = & 0{\cdot}69214 - 1 \\
+ \text{compl.} \log.(1 + 0{\cdot}00366t) = \text{compl.} \log.\ 1{\cdot}0739 & = & \underline{0{\cdot}96903 - 1} \\
\log.\ V & & 2{\cdot}11814 \\
V' & = & 131{\cdot}26.
\end{array}$$

A modification of Bunsen's method has been proposed by Messrs. Williamson and Russell (Proceedings of the Royal Society, vol. ix. p. 218), whereby the effect of any alteration in the barometer or thermometer on the gas during the analysis is entirely eliminated: moreover, the gas operated on is always read off saturated with aqueous vapour, so that no calculations are necessary for reducing the volume to a standard temperature and pressure. The principle on which this simplification depends is, that of always retaining the gas at the same degree of elasticity. If, for instance, a fall of temperature has occurred, then by diminishing the pressure on the gas a certain amount, its elasticity will remain unaltered; and for a rise in temperature, the pressure must be correspondingly increased to retain the gas at the same volume. This equally applies to any alteration in the barometer. The means adopted for ascertaining exactly how much the pressure on the gas has to be increased or diminished for any variations of the barometer or thermometer, is simply to introduce a standard quantity of air into a tube over mercury, and mark off the height of the mercury on the tube, at the normal temperature and pressure; then, at any other temperature or pressure, by raising or lowering the tube in the mercury-trough, so as exactly to bring the mercury again to the same mark, the elasticity of the air is maintained constant. The gas in the eudiometer is always read off at this constant degree of expansion, and this is done merely by raising or lowering it in the trough, until the column of mercury within the eudiometer is of exactly the same height as that in the tube containing the standard amount of air. *Fig.* 58 represents the apparatus used in this method. A B is the tube containing the standard amount of air, and is termed the "pressure-tube:" the upper part of it is six or seven inches long, and of about the diameter of an ordinary Bunsen's eudiometer; the lower part B is of about the same length, but only $\frac{3}{8}$ inch internal diameter. Into this pressure-tube is introduced such a quantity of mercury that, when it is inverted in the trough, the mercury stands at a convenient height in the narow tube; at this point, the mark is made which indicates the height of mercury needed at any temperature or pres-

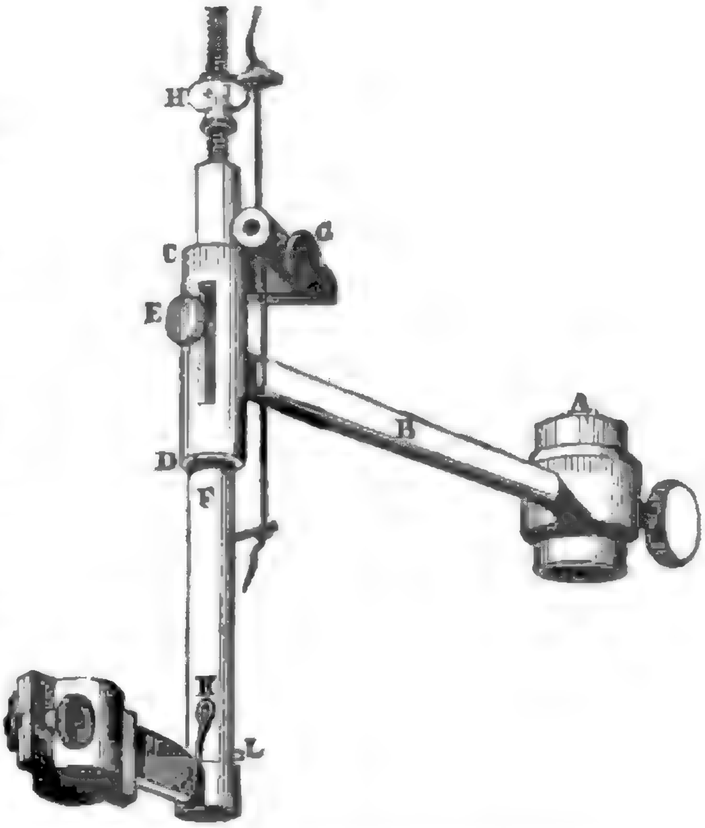
Fig. 58.



sure, to reduce the enclosed air to its original volume. The mercury-trough C D differs from the ordinary form in being provided with a well E, at one end, in which the eudiometer is to be raised or lowered so as to bring the gas it contains to the same pressure as the air in the pressure-tube. Both the eudiometer and the pressure-tube are held in a perpendicular position by means of clamps F and G, which slide on upright rods. Each clamp is provided with a simple kind of slow movement, by which the tube can be raised or lowered by the operator, whilst he is looking through a telescope at a suitable distance.

Fig. 59 is an enlarged view of one of the clamps, which shows more distinctly how the slow movement is produced. A is the part which slides up and down the vertical rod; it is furnished on the inside with a small steel peg, which moves in a groove, thus causing the arm always to remain in the same plane. C D is a tube through which the rod F, carrying the clamp, passes. E is a screw which retains the rod F in its place, and by means of which the friction on the rod passing through the tube can be increased at pleasure. G is a small cylinder fixed to C D; on turning this round to the right or to the left, the string above or below is wound on to it, and consequently the rod F raised or lowered. In order that the heat from the body may not affect the volume of the gases in the tubes, thin iron rods, some six feet in length, are screwed into these cylinders, and rest on the arm carrying the telescope, as shown in *fig.* 58. H is merely an arrangement for tightening the string. K is a peg so placed with regard to the stop L, that when, by turning the clamp round, it is pressed against the stop, the tube is then in the right position for applying the final adjustment and reading off. In operating with this apparatus, the pressure-tube is placed immediately in front of the eudiometer, and the clamp moved up or down the vertical rod till the top of the mercury inside about coincides with the mark on the stem of the tube; in the same way, the eudiometer is so adjusted that the internal column of mercury is of about the same height as that in the pressure-tube. The iron rods are then screwed on, and the whole allowed to cool.

Fig. 59.



The method adopted in reading off the amount of gas is, while looking through the telescope, first to turn the rod connected with the pressure-tube so as to bring the mercury exactly up to the mark on the stem, then raise or lower the eudiometer so that the meniscus of the mercury inside it may coincide precisely with the meniscus in the pressure-tube. This is easily done, as the diameter of the pressure-tube is considerably smaller than that of the eudiometer, and the meniscus in the latter can be clearly seen on both sides of the meniscus of the pressure-tube. It is convenient also to have a second pressure-tube, the stem of which should be about three times as long as that of the one already described. By this means, when only a small amount of gas has to be measured, it can be read off at a greatly reduced pressure, and consequently with greater absolute accuracy. In order to render the reading made with one pressure-tube comparable with those made with the second, it is only necessary to measure the same amount of gas at each of these degrees of expansion, this at once establishes the proportion in which any amount of gas read off, at the greater degree of expansion, for instance, will have to be diminished in order to render it comparable with gas read off at the lower degree of expansion. This method yields very accurate results, and they are obtained with less trouble than by Bunsen's method, and without any tedious calculations.

The method and apparatus next to be described is that proposed by MM. **Regnault** and **Reiset** (Ann. Chim. Phys. [3] xxvi. 333). Its peculiar advantage is, that analyses may be made by it with very much greater rapidity than is possible by either of the methods previously described, and also that it does not require a room to be set apart for gas analysis.

The economy of time is effected in two ways: first, by surrounding the gas-tubes with water, which almost immediately causes their contents to assume the same temperature as that of the external medium; secondly, by the use of liquid reagents instead of solid, which are necessarily used in Bunsen's method.

The form and principle of M. Regnault's apparatus will be easily understood from *figs.* 60 and 61. It consists essentially of two parts, which can be easily joined and separated. In the one part, the gas is subjected to the action of the liquid reagents, and this is termed the laboratory or absorption-tube; in the other, the gas is measured, and it is termed the measuring-tube; these are represented in the figures by *f g*, and *a b*. The measuring tube *a b*, is from 15 to 20 mm. internal diameter. It is divided into millimetres, and terminates above in a fine capillary tube *a r*, while the lower end is luted into a cast iron piece *NN*, having two tubulations, *b* and *c*, and a stopcock *R*. To the second tubulation *c*, is luted a straight tube *c d*, open at both ends, of the same diameter as the tube *a b*, and divided also into millimetres. The stopcock *R* is bored through in two directions at right angles to one another, as shown in *figs.* 62, 63, and 64, so that by turning the key in different positions, communication can be established between the two tubes *a b* and *c d*, or the mercury can be

Fig. 60.

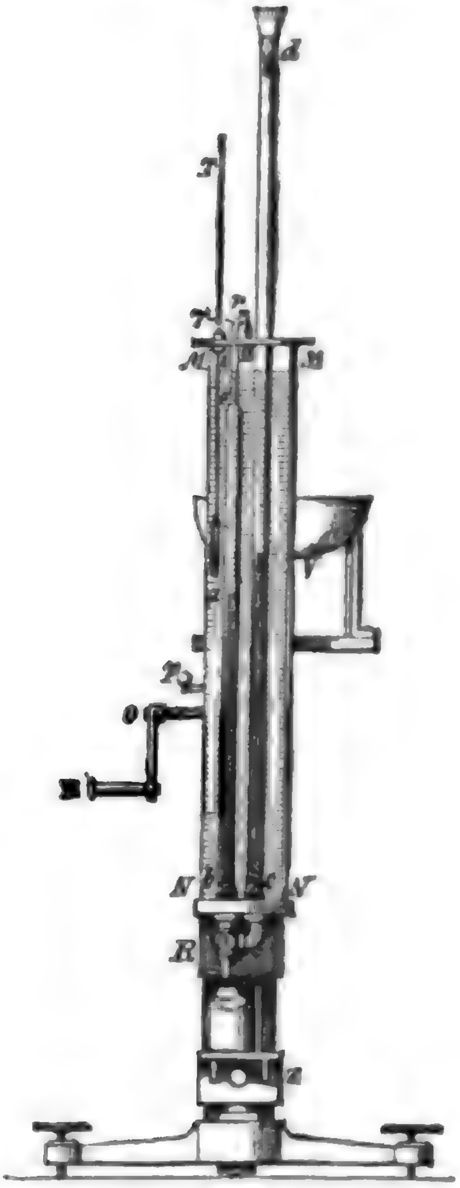
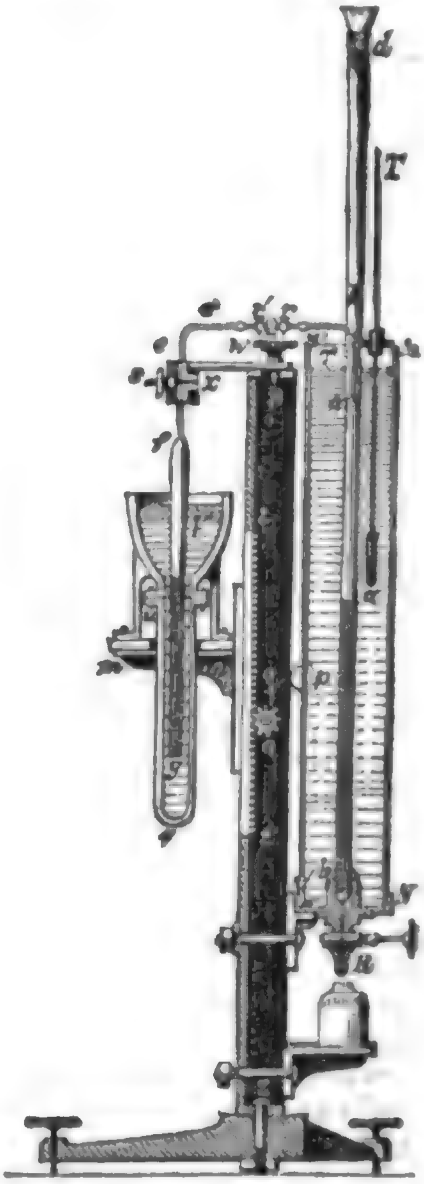
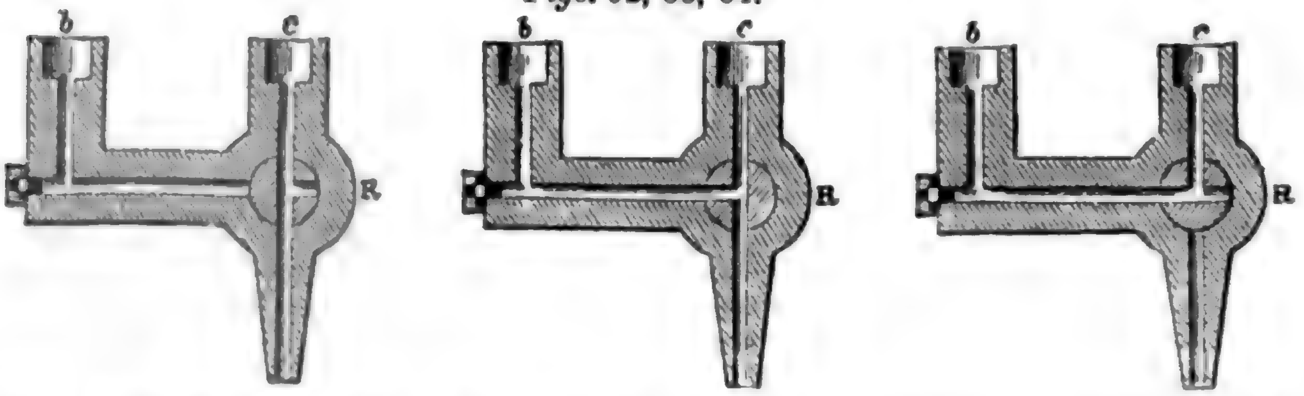


Fig. 61.



Figs. 62, 63, 64.



allowed to flow from either. These tubes are surrounded by a glass cylinder filled with water, in which the thermometer T is immersed. During the analysis, the thermometer must of course indicate a constant temperature; should any alteration have taken place, the original temperature must be restored by the addition of hot or cold water.

The whole apparatus is fixed on a cast-iron stand z z, furnished with levelling-screws. The absorption tube *g f*, is open at the bottom and terminated above by a curved capillary tube *f e r′*. This tube dips into a small mercury trough *V*, of cast iron, or what is still better, gutta-percha, *Figs.* 65 and 66 represent more clearly the form of this trough. When in its place, it rests on a small iron bracket, which by means of the rack *i i*, and the pinion *o*, to which the handle B is attached, is easily moved up and down. It is retained in any position by the rachet *q*, to which, in order to facilitate its working, a weight is fixed, and as this is turned from one side to the other, the rachet is thrown in or out of gear with the pinion. To the ends of the capillary tubes, which terminate the absorption- and measuring- tube, are carefully luted two small steel stopcocks, *r r′*, the ends of which exactly fit each other, and have the shape represented in *fig.* 67, in section. In order to render the joining of the two as air-tight as possible, a little melted caoutchouc is applied to the faces *a b* and *a′ b′*, which are then pressed together as tight as possible by means of a screw clamp, represented in *fig.* 68. The laboratory-tube is held in a vertical position by the clamp *u*, which is lined with cork, and can be adjusted to the required distance from *z z*, by means of the screw *s*. The measuring-tube *a b* is provided with two platinum wires, as in the ordinary eudiometer. The following account given by Regnault (Cours de Chimie, iv. 77) of an analysis of a mixture of air and carbonic acid will perhaps best explain how the apparatus is used.

Fig. 65.

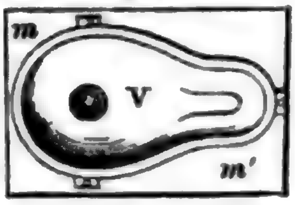
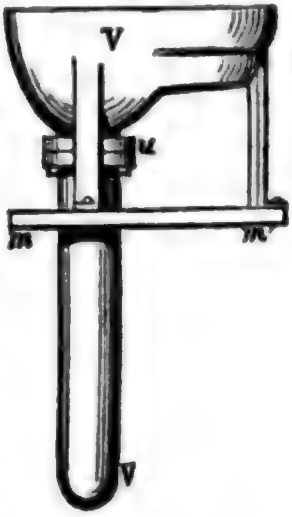


Fig. 66.



The first operation is to fill the measuring-tube: this is done by pouring mercury into the tube *c d*, until it begins to escape through the stopcock *r*, which is then closed. The laboratory-tube is next filled by plunging it into the mercury-trough *V*, the stopcock *r′* being open. To fill the capillary-tube *f e r′*, the best method is simply to apply the mouth to the open end of it and suck the mercury up, then close the stopcock. The tube being now perfectly full of mercury, it is fixed in its place and the clamp screwed on to the stopcocks.

Fig. 67.

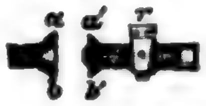
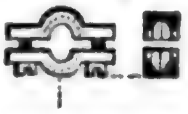


Fig. 68.



The gas to be analysed is now introduced into the laboratory-tube, the trough *V* having been lowered to such a position that the end of the laboratory-tube only reaches to a short distance under the mercury; the gas is then easily passed up into it. This being done, the trough is again raised and the mercury allowed to flow out of the measuring-tube, by which means the gas is forced over into the measuring-tube. When the mercury reaches the capillary tube *f e*, the stopcock *r* is nearly closed, thus causing it to rise but slowly, and when the column of mercury arrives at a certain mark σ on the horizontal part of the capillary tube, the stopcock *r′*, is closed. The level of the mercury is thus brought to a given division α, of the tube *a b*, and the difference of height of the two columns can immediately be read off on the scale of the tube *c d*. The water should be well agitated by blowing air into it through a tube which descends to the bottom of the cylinder. The height of the thermometer and barometer must also be observed.

In order that no calculation should be necessary for estimating the tension of aqueous vapour, the gas is always saturated with moisture; this is done by moistening the sides of the measuring-tube *a b*: the mercury, in passing through, merely removes the excess of water, and always leaves a small quantity adhering to the sides of the tube. Let t be the temperature of the water, which, as before stated, must be stationary during the analysis, f the tension of the aqueous vapour at this temperature; v the volume of the gas; H the height of the barometer; and lastly, h the difference of the height of the mercury in the two tubes. $H + h - f$ is then the elasticity of the gas when dry. Having thus measured the quantity of gas taken, the next operation is to absorb the carbonic acid present. The trough *V* is again lowered and by means of a bent pipette, a single drop of a strong solution of caustic potash is introduced into the laboratory-tube. Mercury is then poured into the tube *c d*, and the stopcock R turned so as to establish communication between the tubes *a b* and *c d*. On opening the stopcocks *r r′*, the gas is then forced back into the laboratory-tube.

As the mercury in it sinks, the caustic potash moistens the sides of the tube, thus exposing a very large absorbing surface. In a few minutes, the whole of the carbonic acid is absorbed; and the absorption may be rendered still more speedy and certain, by raising the trough and opening the stopcock r, so that the gas may again be drawn into the measuring tube and afterwards forced back a second time into the laboratory-tube, thus bringing it in contact with a fresh surface of potash. It has been shown that after this operation has been repeated twice, no appreciable amount of carbonic acid remains unabsorbed. As it is essential that none of the absorbing liquid should ever pass over into the measuring-tube, the error arising from an amount of gas remaining in the capillary tube $f\,e\,r'$, is best eliminated by always making this a constant quantity, which is done by closing the stopcock r', when the column of liquid reagent or mercury arrives at a certain mark σ.

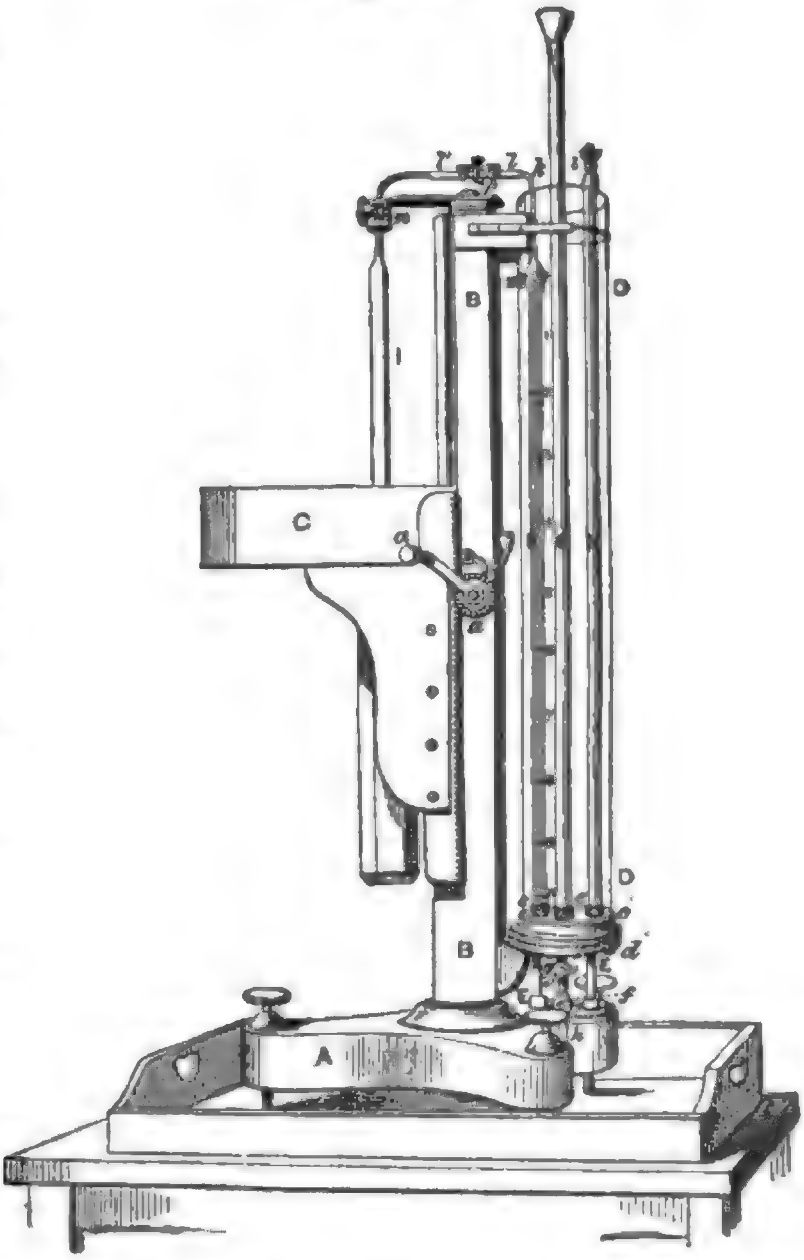
The absorption being completed, the level of the mercury in the tube $a\,b$ is again brought to the mark α, and the difference of height h' of the mercury in the two tubes $a\,b$ and $c\,d$, is read off. H' the height of the barometer, is also noted. If the temperature of the water in the cylinder has changed, it must be restored to the original temperature t, by the addition of hot or cold water. The elastic force then of the gas deprived of carbonic acid and dry, is $H' + h' - f$; and consequently $(H + h - f) - (H' + h' - f) = H - H' + h - h'$, is the diminution of elastic force, caused by the absorption of the carbonic acid; and $\dfrac{H - H' + h - h'}{H + h - f}$ represents the proportion of carbonic acid in the gas when dry.—The proportion of oxygen in the remaining gas has now to be determined. The laboratory-tube is detached, thoroughly washed, and dried, first by means of paper, and afterwards by bringing it into connection with an air-pump. It is then again filled with mercury and fitted on to the measuring-tube. The trough U is now raised, and the stopcock R opened. On now turning the cocks $r\,r'$, the mercury in the laboratory-tube passes into the capillary-tube $a\,r$, and is allowed to proceed as far as a given mark τ; when it reaches this mark, the stopcocks $r\,r'$ are closed. The mercury in the measuring-tube is then again brought to the point α, and the difference of the level h'' and the height of the barometer H'' read off. $H'' + h'' - f$ is therefore the elastic force of the dry gas now in the apparatus, a small quantity (about $\frac{1}{3000}$) of the whole having been lost by detaching the laboratory-tube. This second measurement prevents any inaccuracy thence arising.

A proper quantity of hydrogen is now introduced, and a uniform mixture of the whole produced by passing the gas two or three times backwards and forwards from the laboratory-tube into the measuring tube. When thoroughly mixed, the column of mercury is again brought to the mark τ, and the gas in the measuring tube to the point α. The difference of height h''' of the two columns of mercury is read off, and the height H''' of the barometer. $H''' + h''' - f$ is therefore the elastic force of the mixture of hydrogen, oxygen, and nitrogen. The capillary-tube $r\alpha$, is now completely filled with mercury, so that none of the gas shall escape combustion, and an electric spark passed through the mixture. After the explosion, the stopcocks $r\,r'$ are carefully opened and the gas subjected to a slight pressure, so that the mercury is forced back along the capillary-tube till it arrives at the point τ; the stopcocks are then again closed, and the gas expanded as before to the mark α. Its elasticity will now be represented by $H'''' + h'''' - f$. Consequently $(H''' + h''' - f) - (H'''' + h'''' - f) = H''' - H'''' + h''' - h''''$, is the elastic force of the gaseous mixture which disappeared during the combustion; $\frac{1}{3}(H''' - H'''' + h''' - h'''')$ is the elastic force of the oxygen contained in the dry gas, of which the elastic force was $H'' + h'' - f$; and $\frac{1}{3}\dfrac{H''' - H'''' + h''' - h''''}{H'' + h'' - f}$ is the proportion of oxygen contained in the gas when freed from carbonic acid, whence the proportion of oxygen in the original gas may be easily deduced.

As the gas is made to occupy a constant volume during the whole analysis, this entirely removes the necessity of calibrating any of the tubes. This apparatus may, however, be used in a different way, and then the calibrating of the tube $a\,b$ becomes necessary. In this case, instead of always bringing the gas to a constant volume and reading off the pressure it supports, the pressure is retained constant, and the difference of volume read off. The calibration of the tube $a\,b$ is effected by filling it completely with mercury, and then allowing a small quantity to flow out through the stopcock R, collecting and weighing this, then reading off on the tube the height through which the mercury has fallen. The temperature of the water in the cylinder should be kept constant during the whole operation.

The apparatus of MM. Regnault and Reiset leaves but little to be desired with regard to the rapidity with which analyses can be made; but this rapidity is to a certain extent obtained at a sacrifice of accuracy, considerable change in the bulk of gas operated on being represented by only a small change in the amount of pressure. In a comparison made by Messrs. Frankland and Ward, of the methods of Bunsen and Regnault, it was shown that an error of $\frac{1}{10}$ of a millimetre in the first observation would cause in Regnault's method an error in the percentage amount, seven times as great as would be the case when Bunsen's method was adopted. There is also considerable practical difficulty in maintaining the water in the cylinder at precisely the same temperature for any length of time together.

Fig. 69.



Messrs. Frankland and Ward have constructed (Chem. Soc. J. vol. vi. p. 197) another form of apparatus for the analysis of gases, which, in mechanical construction and in the method of working it, is very similar to the apparatus of Regnault and Reiset, but possesses at the same time many important advantages over it. The effect of atmospheric pressure on the gas is entirely removed; the principle adopted in measuring the amount of gas yields very accurate results; the gas may be expanded to almost any amount, rendering this apparatus one of considerable importance. *Fig.* 69 is a drawing of the apparatus. "It consists of the tripod A, furnished with the usual levelling screws, and carrying the vertical pillar B B, to which is attached on the one side the movable mercury-trough C, of gutta-percha, with its rack and pinion *a a*, and on the other the glass cylinder D D, with its contents. The cylinder is 36 inches long, and 4 inches internal diameter; its lower extremity is firmly cemented into an iron collar *c*, the under surface of which can be screwed perfectly water-tight upon the bracket-plate *d*, by the interposition of a vulcanised caoutchouc ring. The circular iron plate *d* is perforated with three apertures, into which the caps *e e e* are screwed, and which communicate below the plate with the T-piece E E. This latter is furnished with a double-waycock *f*, and a single-waycock *g*, by means of which the tubes cemented into the sockets *e e e*, can be made to communicate with each other, or with the exit pipe *h* at pleasure." F, G and H are three glass tubes which are firmly cemented into the caps *e e e*. F and H are each 15 to 20 mm. internal diameter, and to avoid any difference in the capillary action, are selected of as nearly the same bore as possible. The tube G is somewhat wider, and may be continued to any convenient height above the cylinder. H is accurately graduated into millimetres, and is furnished at the top with a small funnel *i*, into the neck of which a glass stopper, about 2 mm. in diameter, is carefully ground. The tube F terminates at its upper extremity in the capillary-tube *k*, which is carefully cemented into the small steel stopcock *l*. F has also fused into it at *m* two platinum wires, for the passage of the electric spark. After this tube has been firmly cemented into the cap *e*, its internal volume is accurately divided into ten equal parts. This is done first by filling it with mercury from the supply tube G, up to its junction with the capillary tube *k*, and then allowing the mercury to run off through the nozzle *h*, until the highest point of the meniscus stands at the division 10 previously made, so as exactly to coincide with the zero of the millimetre scale on H. The weight of the mercury thus run off is carefully determined, and the tube is again filled as before, and divided into ten equal parts, by allowing the mercury to run off in successive tenths of the entire weight, and marking the height of the top of the meniscus after each abstraction of the metal, by screwing a small copper ring on to the tube at that point. By using proper precautions with regard to temperature, &c., an exceedingly accurate calibration can be made in this way. In practice, however, it is found much easier to make the calibration in the following manner. The ten copper rings are screwed on to the tube first, at about equal distances apart, but without any relation to the capacity of the tube, which is afterwards ascertained by expanding the same volume of gas down to each of the ten divisions, and reading off the height of the column of mercury in the tube H in each instance. The way in which the laboratory tube J is joined to the rest of the apparatus is precisely similar to that adopted by MM. Regnault and Reiset, and already described.

When the instrument is thus far completed, it is requisite to ascertain the height of each of the nine upper divisions on the tube above the lowest or tenth division; this is very accurately effected in a few minutes by carefully levelling the instrument, filling the tube G with mercury, opening the cock *l*, and the stoppered funnel *i*, and placing the cock *f* in such a position as to cause the tubes F H to communicate with the supply-tube G. On now slightly turning the cock *g*, the mercury will slowly rise in each of the tubes F and H; when its convex surface exactly coincides with the ninth division on F, the influx of metal is stopped, and its height in H accurately observed; as the tenth division on F corresponds with the zero of the scale upon H, it is obvious that the number thus read off is the height of the ninth division above the zero point. A similar observation for each of the other divisions upon F completes the instrument.

Before using the apparatus, the large cylinder D D is filled with water, and the inside of the tubes F and H are once for all moistened with distilled water, by the introduction of a few drops into each, as in Regnault's apparatus. The three tubes being then placed in communication with each other, mercury is poured into G until it rises into the cup *i*, the stopper of which is then firmly closed. When the mercury begins to flow from *l*, that cock is also closed. The tubes F and H are now apparently filled with mercury, but a minute and imperceptible film of air still exists between the metal and the glass: this is effectually got rid of by connecting F and H with the exit-tube *h*, and allowing the mercury to flow out until a vacuum of several inches in length has been produced in both tubes. By allowing the instrument to remain thus for an hour, the whole of the film of air above mentioned will diffuse itself into the vacuum, and will become visible as a minute bubble in each tube, on allowing the vacuum to be filled up from the supply-tube G. By opening for a moment the stopper *i* and the cock *l*, whilst G is full of mercury, these bubbles are expelled. The absorption or laboratory-tube I being then filled with quicksilver, and attached to *l* by the screw clamp, the instrument is ready for use.

The method of introducing the gas, applying the absorbents, and passing the gas from one tube to the other, is in this apparatus so precisely similar to that adopted in using Regnault's apparatus, and before described, that it need not be further dwelt upon. The method of reading off the amount of gas is, however, different, and requires a few words of explanation. When the gas has been passed over into the tube F, mercury is allowed to flow out of the stopcock *f*, until a vacuum of two or three inches in length is formed in H, and the metal in F is just below one of the divisions; the cock *f* is then reversed, and the mercury very gradually admitted from G until the highest point in F exactly corresponds with one of the divisions on that tube; that this is really the case, must afterwards be ascertained by viewing it through a telescope. The height of the mercury in the tube H is then read off. If the division on the tube F, to which the gas has been expanded is, for instance, the fourth, then, from the number read off on the tube H must be deducted the height of this fourth division above the zero point of the tube. The remainder will express the volume of the gas; but in order to compare this with subsequent readings made at other divisions upon F, the number thus obtained, which represents the pressure of the gas, is reduced to what it would have been had the gas been expanded to the tenth division of F. This is very simply done, by merely multiplying the number representing the pressure of the gas by a fraction whose denominator is 10, and numerator the number of the division to which the gas has been expanded; thus, in the case above cited, the multiplier would be 0·4.

The following are the results of an analysis of air made by Messrs. Frankland and Ward.

Volume of air used. (Determined at fifth division on F.)

Observed height of mercury in H	673·0 mm.
Height of fifth division above zero	383·0
Corrected pressure of gas	290·0
	·5
Corrected pressure of gas at tenth division	145·0

Volume after the admission of hydrogen. (Determined at sixth division.)

Observed height of mercury in H	772·3 mm.
Height of sixth division above zero	304·0
Corrected pressure of gas	468·3
	·6
Corrected pressure of gas at tenth division	280·98

Volume after explosion. (Determined at fifth division.)

Observed height of mercury in H	763·3
Height of fifth division above zero	383·0
Correct pressure of gas	380·3
	·5
Corrected pressure of gas at tenth division	190·15

Results.

Volume of air used	145·00
Volume of oxygen	30·276

Hence:

Nitrogen	79·120
Oxygen	20·880
	100·000

Greatly superior as this form of apparatus is to that of Regnault, and capable as it is of yielding accurate and rapid results, still there are defects in it which detract somewhat from its practical value. The principal of these is the great difficulty there exists in always maintaining the apparatus in a perfectly air-tight condition, especially as the stopcocks *l′* and *l* have to be joined and separated once or twice during an analysis. Considerable inconvenience has also been found to arise from the very fragile nature of the laboratory-tube; this, even when full of mercury, is only supported by the capillary tube, to which it is fused, and consequently the slightest blow or pressure upon it is apt to cause it to separate at this point of junction. Some difficulty is also experienced in keeping the water in the cylinder at exactly the same temperature during the whole course of the analysis. Regnault, as before stated, suggests adding hot or cold water till the required temperature is obtained; this is an operation which takes considerable time, and without much care is likely to lead to fallacious results. Dr. Frankland has proposed using a stream of water direct from the street main, which enters the cylinder at the bottom, and is allowed to flow off by an exit-tube near the top. This is a great improvement upon Regnault's method, but even with this arrangement, slight variations occasionally occur.

Having now described the principal forms of apparatus used in the analysis of gases, we shall proceed to state the methods to be adopted for the separation and quantitative estimation of the different contituents which may occur in a gaseous mixture. Gases which have a strong affinity for any particular reagent, are estimated directly by introducing the reagent into the absorption-tube; but since many gases are not absorbable in this manner, another and indirect method has to be adopted, as for instance, in the case of hydrogen, which is estimated by exploding it with oxygen and observing the diminution of volume thence ensuing.

The following list will show which gases are estimated directly and which indirectly. Two of the number, namely oxygen and carbonic oxide, will be found in both lists, as they can be estimated by either method.

Gases estimated by the direct method.

Hydrochloric acid (anhydrous).
Hydrobromic acid.
Hydriodic acid.
Hydrofluoric acid.
Hydrosulphuric acid.
Sulphurous acid (anhydrous).
Carbonic acid (anhydrous).
Oxygen.
Carbonic oxide.
Olefiant gas.
Nitric oxide.

Gases estimated indirectly.

Nitrogen.
Oxygen.
Hydrogen.
Carbonic oxide.
Light carburetted hydrogen.
Ethyl.
Methyl.

The gases estimated by absorption may, for analytical purposes, be conveniently divided into three groups.

1st Group: — *Hydrochloric acid; Hydrobromic acid; Hydriodic acid.* These are absorbable by means of sulphate of sodium.

2nd Group: — *Hydrosulphuric acid; Sulphurous acid; Carbonic acid.* These are absorbed by caustic potash, but not by sulphate of sodium.

3rd Group: — *Oxygen; Nitric oxide; Carbonic oxide; Olefiant gas.* These are neither absorbed by sulphate of sodium nor by caustic potash. With regard to the manner of applying the reagent, if the apparatus of Regnault or Frankland be used a few drops of a very strong solution of the reagent are introduced into the laboratory-tube, by means of a bent pipette, as little of the liquid being used as possible, to prevent any appreciable loss arising from its absorbing power. But in using Bunsen's method, or that proposed by Williamson and Russell, the reagent must be introduced in a solid form if possible, or if necessarily a liquid, some porous substance must be saturated with it.

Estimation of the Gases of the 1st Group.—The sulphate of sodium is introduced into the gas by first melting it in its water of crystallisation, and then dipping into it the end of a platinum wire which has been bent into a short coil; this is repeated several times until a ball of the sulphate of sufficient size is obtained. If much of these acids is believed to be present, the ball should be of a large size, or else the sulphate of sodium is apt to become deliquescent, and run down the sides of the tube. All aqueous vapour must also be carefully removed from the gas before introducing the sulphate of sodium. This is best accomplished by means of a ball of phosphoric acid, which may easily be made by dipping the coiled end of a platinum wire into hot liquid phosphoric acid; a drop adheres to the wire, and then as the acid cools the size of the ball is increased to about that of a large pea, by turning it round in the viscous melted mass. The thickness of the platinum wires used in these experiments should be such that the balls of reagent may be easily pushed into the eudiometer without the wire bending. Great care must also be taken that the surface of the ball is as smooth as possible, or adhering air will be introduced into the gas, and some of the gas removed on withdrawing the ball. Oxide of bismuth or zinc may also be used for absorbing the members of this group. A ball of these substances is best made by applying the moist oxide to the end of the platinum wire, and then igniting it in the flame of a spirit-lamp. The results obtained with these absorbents are, however, generally not quite so accurate as those obtained with the sulphate of sodium. The different members of this group cannot be separated by any eudiometrical process. If several of them occur together, the ball of sulphate of sodium used for their absorption must afterwards be dissolved in water, and the solution analysed in the ordinary way.

Estimation of the Gases of the 2nd Group.—As stated above, the members of this group are all absorbed by caustic potash. A ball of this substance is made by fusing caustic potash and adding sufficient water to render it, when cold, soft enough to receive an impression from the nail; the end of the platinum wire bent into a coil is then placed in a bullet-mould of convenient size, and the fused potash poured in. If the ball should adhere firmly to the mould when cold, as is sometimes the case, heat must be applied; it will then easily be removed. On using a potash-ball for absorbing gases, it must always be moistened with water before introducing it into the gas. When much gas has to be absorbed by this means, the potash-ball should, after some hours, be removed from the eudiometer, washed, and then again introduced. It should be allowed to remain some four to six hours in contact with the gas, in order to ensure complete absorption.

Hydrosulphuric acid.—This gas is best absorbed by means of a ball of peroxide of manganese. The manganese is very finely powdered and made into a thin paste, with water; this is introduced into a bullet-mould with the platinum wire in it, and then dried on a hot sand-bath. If, however, this ball were at once introduced into a gaseous mixture, it would, from its porous nature, absorb an appreciable amount of other gases besides hydrosulphuric acid. To obviate this, the ball before being used should be thoroughly moistened with a syrupy solution of phosphoric acid; care must however be taken that this does not soften the ball, or it may fall to pieces on attempting to introduce it into the eudiometer. There is also another method of estimating this gas, but it is applicable only when sulphurous acid is not present. A potash-ball containing a large quantity of water, but not moistened externally, so that, on withdrawing it, none of the potash remains in contact with the mercury, is introduced into the eudiometer: this absorbs the hydrosulphuric and carbonic acid, if any is present. "Distilled water acidulated with acetic acid, is then boiled in two flasks until all the dissolved air has been removed; the contents of one flask is then poured, whilst boiling, into the other, filling it up to the top of the neck. The flask is then well closed with a cork covered with a plate of caoutchouc, so that no bubble of air is left between the liquid and the caoutchouc plate. As the liquid cools, the cork is pushed further into the neck, in order to prevent the formation of a vacuous space and the possible entrance of air. The ball of potash, cut off from its platinum wire immediately on withdrawal from the gas, is allowed to dissolve in this liquid when cool, and a few drops of a clear solution of starch are added." * The amount of hydrosulphuric acid present is then determined by means of a standard solution of iodine. In order to free the determination from any error which might arise from impurities in the potash, the experiment is repeated exactly in the same way with a ball of the same potash, but containing no sulphide of potassium. The amount of iodine used in this case is then subtracted from the amount used in the former experiment.

Sulphurous acid.—This gas is estimated by exactly the same methods as those adopted for hydrosulphuric acid.

Carbonic acid.—Caustic potash is the reagent always used in determining the amount of this gas in any mixture. The method of preparing the ball, and the necessary precautions in using it, were described when speaking of potash as the general absorbent of this group.

Estimation of the Gases of the 3rd Group.—This group consists of four gases not absorbable either by sulphate of sodium or by caustic potash. They will be treated in the order in which they would have to be separated from a gaseous mixture.

Oxygen.—This gas may be estimated either directly or indirectly, the method to be adopted in any particular case depending on the quantity present, and the nature of the gases with which it is mixed. If other combustible gases are present, or if there is only a small amount of oxygen in the mixture, it is always better to estimate it directly. The method to be adopted in determining it indirectly will be described further on. Phosphorus was formerly the substance generally used to free a gaseous mixture from oxygen; but owing to the tension of the vapour of the phosphorus acid formed, the difficulty of removing it, and the action which many gases have in preventing the union of phosphorus and oxygen at ordinary temperatures, the use of this reagent is apt to lead to incorrect results. A much better method of absorbing oxygen is to use pyrogallate of potassium. It may be introduced into the absorption-tube either by means of a papier-maché ball, or if liquid reagents are used, a few drops of a strong solution of the acid are first introduced and some caustic potash added to it.

The papier-maché ball is made by thoroughly macerating some bibulous paper in water, then, having introduced the platinum wire into a bullet mould, and tied the two handles together so that it cannot open, as much of the pulp is forced in round the platinum wire as possible. After being dried on a sand-bath, a hard compact ball is thus formed; this is thoroughly saturated with the pyrogallate of potassium, and then immediately introduced into the gas. The absorption of oxygen by this means is not always very rapid, and it is often necessary to withdraw the ball from the eudiometer, again saturate it with the pyrogallate solution, and introduce it a second time into the eudiometer.

Nitric oxide.—This gas and oxygen can, of course, never occur together. The best method of estimating it, is first to convert it into nitrous acid and then absorb the acid thus formed, by potash. For this purpose, a few bubbles of oxygen are introduced into the gas in the absorption-tube, and afterwards potash, either in the solid or liquid form. When the absorption is complete, a further quantity of oxygen is added; if after this addition, no absorption is caused by the potash, then an excess of oxygen is present, but if absorption again takes place, more oxygen must be added. Having in this manner ascertained that the whole of the nitric oxide is removed, it then only remains to absorb the excess of oxygen present, by means of pyrogallate of potassium, as before described. When this gas is mixed with nitrous oxide, olefiant gas, or hydride of ethyl, this method, according to Dr. Frankland, gives good results; but in the presence of other hydrocarbons, it is possible that the nitrous acid and peroxide of nitrogen might exercise an oxidising action on them, and thus vitiate the results. Protosulphate of iron was also formerly used as an absorbent for nitric oxide; but it does not yield very satisfactory results.

Carbonic oxide.—Like oxygen, this gas is also estimated sometimes directly, sometimes indirectly. At present, its direct estimation only will be treated of. This is best effected by means of a concentrated solution of subchloride of copper. A papier-maché ball, similar to the one used for the pyrogallate of potassium, is the best means of introducing the solution into the absorption-tube, when the liquid alone cannot be used. This gas is, however, generally estimated by the indirect method, which yields extremely accurate results.

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* Bunsen's Gasometry, p. 86.

Olefiant gas.—This gas, together with all others of the formula C^nH^{2n}, is easily and rapidly absorbed by means of anhydrous sulphuric acid, dissolved in about an equal weight of the monohydrated acid. This mixture is best introduced into the gas by saturating a coke bullet with it. The bullet is made by taking a finely powdered mixture of equal parts of cannel coal and coke, or anthracite coal, and after introducing the platinum wire, compressing as much as possible of the mixture into the bullet-mould, which is then carefully and slowly heated to redness. By this means a hard and compact ball is easily formed. Before introducing it into the acid mixture, it should always be warmed to expel any moisture present, and after being saturated with acid, must be introduced into the gas as quickly as possible. The ball, when withdrawn after some hours from the eudiometer, should still give off dense white fumes, on coming in contact with air, thus showing that an excess of acid was present. Owing to the tension of the sulphuric acid introduced, and the sulphurous acid which is formed, the bulk of gas in the absorption-tube generally increases instead of diminishes, on first introducing the coke bullet. To remove the acid vapours thus formed, after withdrawing the coke bullet, a potash-ball must be introduced.

After the coke bullet has been withdrawn, although at present there is no direct method known for separating and estimating singly the different hydrocarbons having the general formula C^nH^{2n}, still, if two of them occur together, the amount of each can be easily determined by an indirect method to be described further on.

Gases estimated indirectly.—In estimating the gases belonging to this class by Bunsen's method, the long eudiometer is always used. After having completed the absorptions in the short tube, a portion only of the gas is introduced into the eudiometer, the amount depending on the nature of the gases operated on. In most cases, a volume occupying about 120 mm. on the scale, will be found convenient. Certain precautions are, however, necessary in using the tube for exploding gases. In order to close securely the open end of the eudiometer, so that no gas may be forced out at the moment of explosion, a small round piece of cork or wood, of rather greater diameter than the eudiometer, is covered on one side with a thick piece of caoutchouc, and the other is so shaped that it rests firmly on the bottom of the mercury-trough. Before exploding the gas, the eudiometer is tightly pressed down on to the caoutchouc, and held firmly in this position by a wooden arm pressing on the top of it. In order to prevent any air adhering to the surface of the caoutchouc, which, after the explosion, owing to the diminution of pressure, might be sucked up into the eudiometer, the caoutchouc, before introducing it under the mercury, should always be moistened with a solution of corrosive sublimate, which causes the mercury to adhere closely to it, and entirely removes the possibility of any air being introduced into the eudiometer.

It will be found convenient, as it saves much time and calculation, to form for the eudiometer a table of volumes. This is done by introducing a small tube full of air, and then reading off the height at which the mercury stands; a second tube full is then introduced, and the height of the mercury again read off, and so on till the eudiometer is filled with air. By noting down the level of the mercury in the tube after each addition of air, the successive differences of these numbers express the bulk of the same amount of gas under different pressures, these pressures depending on the height of mercury in the eudiometer.

The following is part of a table formed in this way:—

Vols.	Height of mercury.	Differences.
1	53	2
2	96	43
3	131	35
4	161	30
5	187	26

The use of this table is to enable the operator to see at a glance the amount of gas to be added when the mixture is to be exploded; for instance, suppose the height of the mercury in the eudiometer was 131, and the nature of the gas such that about 2 vols. of oxygen had to be added, in order that an explosion of the proper degree of intensity should take place; by referring to this table the operator would see at once that oxygen must be added till the mercury falls to 187. As the object of the table is only to show about how much gas has to be added under different circumstances, any great degree of accuracy in forming it is not necessary. The readings-off of the heights of the mercury, after each addition of air, may be made without the telescope, and any alteration in the heights of the thermometer and barometer during the operation need not be taken into account.

The explosion of the gaseous mixture is best effected by means of an electric spark, for obtaining which, a small Leyden jar is charged from an electrophorus or an electrical machine, or else by the still simpler method adopted by Bunsen, which consists merely in rubbing a large porcelain tube with a piece of silk on which some amalgam is spread. Ruhmkorff's coil may also be advantageously used for exploding gases.

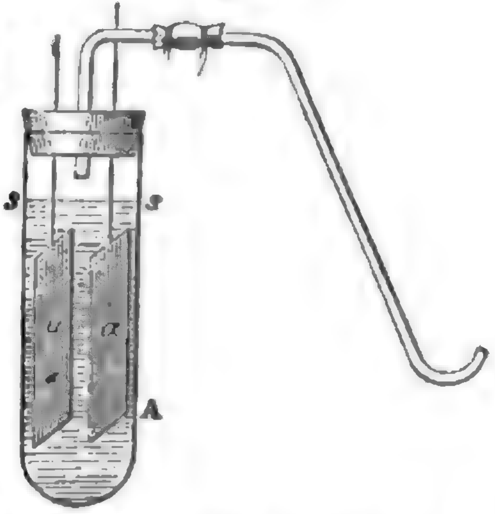
Before filling the eudiometer with mercury, a drop of water should always be introduced into the top of it, so that the volume of gas may be read off saturated with aqueous vapour.

Nitrogen.—This gas, from its incombustible nature, can, of course, be estimated only by removing all others with which it is mixed, and measuring the amount remaining; but although it cannot be made to combine with oxygen, so as to remove it entirely from a mixture, still, as is well known, the oxidation of it does often take place to a considerable extent, and, if not properly guarded against, is likely to lead to very serious errors in the analysis of gases. In fact, the discordant and incorrect results obtained by the earlier experimenters on the composition of the atmosphere, did no doubt arise in great measure from this cause. It became then a point of great importance to ascertain whether this oxidation of nitrogen always took place when mixtures containing it were exploded, and if not, what must be the relative amounts of combustible and incombustible gases present, in order that no trace of any oxide of nitrogen should be formed. We are indebted to Professor Bunsen for a series of experiments on this subject, which remove all uncertainty in the matter. By taking mixtures of atmospheric air and electrolytic detonating gas in different proportions, he has clearly shown that when for every 100 volumes of non-combustible gas 26 to 64 volumes of combustible gas are taken, no oxidation of the nitrogen takes place.

To determine the presence of nitrogen in a mixture, the following is the process to be adopted:—Having removed all absorbable gases and measured off a suitable quantity in the eudiometer, some pure oxygen is introduced, and the volume of gas again measured. An electric spark is now passed through the mixture. Even if no diminution of volume should ensue, it cannot be assumed that the gas was pure nitrogen, as the combustible constituents may have existed in so small a quantity that the gas was not of itself explosive. In order to ascertain whether this was the case, about 40 volumes of electrolytic detonating gas must be added for every 100 volumes of the incombustible gas. If, after the explosion which then ensues, the volume of gas still remains unaltered, only pure nitrogen could have been present in the gas examined.

The electrolytic gas above-mentioned may be prepared by means of the apparatus represented in figure 70. The tube A is an ordinary test-tube of rather strong glass, filled to the level *s s*, with distilled water freed from air by boiling, and acidulated with a few drops of sulphuric acid. The open end of the tube is closed with a cork provided with a gas-delivery tube, and having two platinum wires passing through it, to the ends of which are attached platinum plates, serving as electrodes. When the outer extremities of the wires are connected with the poles of a voltaic battery of two of Bunsen's elements, and the portions of gas evolved in the first quarter of an hour are allowed to escape, a chemical mixture of 2 vols. hydrogen and 1 vol. oxygen is afterwards obtained, which disappears completely on explosion, so that there is no necessity to measure the amount of it mixed with any other gas. Time must, however, be allowed for it to diffuse itself through the mixture already in the eudiometer; for this purpose, half to three quarters of an hour should be allowed to elapse, after the introduction of this gas, before the explosion takes place, and the eudiometer should be well agitated.

Fig. 70.



Oxygen.—By exploding the mixture containing this gas with an excess of hydrogen, the quantity present may be very accurately determined, care being taken that the amount of explosive gas bears a proper relation to the total amount present, so that the detonation is not so violent as to endanger the safety of the tube or oxidise the nitrogen if present, and also not too feeble, as in that case oxygen may escape combustion. One-third of the total amount of contraction caused by the explosion is the quantity of oxygen which was present. The hydrogen used in these experiments may be generated in a small flask from pure zinc and dilute sulphuric acid. To remove any traces of carbonic and hydrosulphuric acids, and to prevent sulphuric acid being carried over mechanically, the gas, as it is evolved, should be made to pass through a tube containing caustic potash. The evolution of gas should always be allowed to take place for five or ten minutes before any of it is passed up into the eudiometer.

For very exact experiments, the hydrogen should be obtained by another process, which yields an absolutely pure gas, namely, from the electrolytic decomposition of water. For the generation of this gas, an apparatus similar in form to that used for obtaining the detonating gas (*fig.* 70), may be used. Instead, however, of two platinum plates, only one is used, and the positive pole consists of a platinum wire melted into the decomposing cell at the bottom, and there brought in contact with a layer of mercury amalgamated with zinc. The acid liquid is of the same degree of strength as in the former apparatus. On now passing the current of a battery through it in the proper direction, pure hydrogen is evolved, and is dried by passing through a small vessel containing sulphuric acid, or a tube containing chloride of calcium.

Hydrogen.—The method of estimating this gas is precisely the reverse of that adopted for the estimation of oxygen. The amount of hydrogen present is represented by $\frac{2}{3}$ of the contraction caused by explosion. The oxygen added is best prepared from powdered chlorate of potassium, contained in small retorts of about the capacity of eight or ten cubic centimetres.

These little retorts are easily made by blowing a bulb at the end of a piece of glass tubing, then introducing the powdered chlorate of potassium, and afterwards bending the tube a little above the bulb, so as to give it the form of a retort. The open end should also be bent upwards, in order that it may be introduced into the eudiometer. The air is, of course, first thoroughly expelled by evolving a considerable amount of gas before any is allowed to enter the eudiometer.

Carbonic Oxide.—The method of estimating this gas by absorption has already been explained; it is, however, most accurately, and in most cases most easily estimated by exploding it with oxygen, and then absorbing the carbonic acid formed by means of potash.

Light Carburetted Hydrogen (Marsh-gas).—This gas is also estimated by exploding it with oxygen, and measuring the contraction which has taken place and the amount of carbonic anhydride formed. This gas and all hydrocarbons containing their carbon and hydrogen, as they do in a condensed form, require much greater dilution with non-combustible gases, in order to modify the violence of the explosion, and prevent the oxidation of any nitrogen which may be present. Pure light carburetted hydrogen should be diluted with from 8 to 12 volumes of air and 2 of oxygen, in order that it may be exploded so as to yield accurate results. The object of using air instead of merely oxygen as the diluent is, that if the gas has afterwards be examined for nitrogen, the amount of oxygen which would be present would probably be so large that the eudiometer could not contain sufficient hydrogen to explode it.

Ethyl, Methyl, &c.—These hydrocarbons are easily estimated by simple combustion with oxygen, and measuring the amount of carbonic acid formed, care only being taken that they are sufficiently diluted with incombustible gas. To pure ethyl some 20 times its volume of air should be added, and 6 or 7 volumes of oxygen. Methyl, on the other hand, requires only about 8 volumes of air and 2 or 3 of oxygen. In operating with a mixture which may contain any of these gases, and of entirely unknown composition, the best method of proceeding is to add at first so much air and oxygen that even if the whole of the gas were ethyl, an explosion of not undue violence would take place. If the gas should not explode on passing the spark through it, then a small quantity of electrolytic gas or hydrogen must be added. In this way all danger of a violent explosion may be avoided. The solubility of the gases in strong alcohol may sometimes be examined with advantage, in order to ascertain roughly what is the composition of the gas operated on, and consequently how much diluent it is necessary to add. 1 volume of alcohol will dissolve some 18 volumes of ethyl, while of methyl and hydride of ethyl it dissolves only about its own volume. With regard to these two gases, methyl and hydride of ethyl, since they are isomeric, and in equal volumes contain the same amount of carbon and hydrogen, they cannot be distinguished by any eudiometrical process.

The methods adopted for calculating the composition of the gas from the data which have been thus obtained, are as follows:—With the gases that are estimated directly the nature of the calculation is easily understood. By taking a definite example, the method used in calculating the amount of combustible gases in a mixture will be rendered very obvious. Suppose then that the gas introduced into the long eudiometer contains hydrogen, carbonic oxide, light carburetted hydrogen, and nitrogen. Oxygen would be introduced, the mixture exploded, and the carbonic acid formed absorbed; then to determine the amount of nitrogen present, hydrogen must be added in excess, and the mixture again exploded to remove the oxygen remaining.

Let a be the amount of gas in the long eudiometer,
b „ „ after the addition of oxygen,
c „ „ after the explosion,

Let d be the amount of gas after the absorption of the carbonic acid,
e ,, ,, after the addition of hydrogen,
f ,, ,, after explosion.

From these observations the following data are deduced: —

A, the volume of combustible gas. C, the volume of carbonic acid formed.
B, ,, oxygen consumed. D, ,, nitrogen present.

$\frac{e-f}{3}$ represents the amount of oxygen which remained unconsumed by the first explosion. If this quantity be deducted from d, the remainder is evidently the amount of nitrogen present.

$$D = d - \frac{e-f}{3}$$

A, the volume of combustible gas which was present, is found by deducting the amount of nitrogen from the original volume of the gas, thus:—

$$A = a - \left(d - \frac{e-f}{3}\right)$$

By subtracting the amount of oxygen $\frac{e-f}{3}$ consumed in the second explosion from the amount originally added, we obtain B, the amount consumed by the combustible gas, thus:—

$$B = b - a - \frac{e-f}{3}$$

The amount of carbonic anhydride formed, is:

$$C = c - d.$$

The values of A, B, and C being thus known, it will be possible to calculate from them that of the three unknown quantities:

x the volume of hydrogen
y ,, ,, light carburetted hydrogen
z ,, ,, carbonic oxide

On undergoing combustion the hydrogen and carbonic oxide combine with half their volume of oxygen, whereas the marsh-gas requires twice its volume; and further, both the carbonic oxide and marsh-gas on combustion produce a volume of carbonic acid equal to their original volume. These data give, then, the three following equations:—

$$\begin{aligned} x + y + z &= A \\ \frac{x}{2} + \frac{z}{2} + 2y &= B \\ y + z &= C \end{aligned}$$

and from these may be deduced the value of x, y, and z—

$$\begin{aligned} x &= A - C \\ y &= \frac{2B - A}{3} \\ z &= C - \frac{2B - A}{3} \end{aligned}$$

Thus is obtained the quantity of these gases present in the mixture. If another combustible gas had been present, its amount might also have been determined by estimating the water produced by the explosion as well as the carbonic acid; or else it might be determined by previously removing the carbonic oxide by subchloride of copper in the manner already described. The aqueous vapour in a gas is estimated by placing the eudiometer within a larger tube, and filling the space between the two with steam, the heat from which, as the gas is under a diminished pressure, is quite sufficient to convert the whole of the water into vapour.

If two members of the olefiant gas series C^nH^{2n} should occur together, the quantity of each present may be indirectly estimated in the following way:—A complete analysis of the gas must be made in the ordinary manner, absorbing the olefiant gases by fuming sulphuric acid, and exploding the combustible gases with oxygen. A second analysis must afterwards be made; but, instead of introducing sulphuric acid to absorb the olefiant gas, oxygen is added, and the whole exploded. The difference in the amount of the carbonic acid formed, and in the contraction which has taken place after the explosion, is evidently due to the olefiant gases present.

Let volume of olefiant gases = A
" " carbonic acid formed = B
" " contraction on combustion = C

If the two gases are, for instance, believed to be ordinary olefiant gas and butylene, then, since 1 volume of olefiant gas gives 2 volumes of carbonic acid, and 2 volumes contraction, and 1 volume of butylene gives 4 volumes of carbonic anhydride and 3 volumes contraction, then, if x represent the former gas, and y the latter—

$$x + y = A$$
$$2x + 4y = B$$
$$y = \frac{B - 2A}{2}$$
$$x = A - \frac{B - 2A}{2}$$

The contraction C gives also a third formula:

$$2x + 3y = C$$

which, combined with the first equation, gives the values of x and y to be:

$$y = C - 2A$$
$$x = A - C + 2A$$

The values obtained from both these sets of equations ought to agree.

By means of the following table, it will be easy to ascertain what formulæ have to be adopted in calculating the amount of combustible gases present in any mixture.*

Name of Gas.	Volume of Gas.	Volume of Oxygen consumed.	Decrease of volume after explosion.	Vol. of carbonic anhydride produced.
Hydrogen	1	0·5	1·5	0
Carbonic oxide	1	0·5	0·5	1
Hydride of methyl	1	2·0	2·0	1
Olefiant gas	1	3·0	2·0	2
Methyl	1	3·5	2·5	2
Hydride of ethyl	1	3·5	2·5	2
Propylene	1	4·5	2·5	3
Butylene	1	6·0	3·0	4
Ethyl	1	6·5	3·5	4

If the gaseous mixture consisted, for instance, of hydrogen, carbonic oxide, and nitrogen, and if A = the volume of the gas, C the diminution after explosion, and D the amount of carbonic acid produced, then taking x = hydrogen, y = carbonic acid, and z = nitrogen, we have:

$$x + y + z = A$$
$$\frac{3}{2}x + \frac{y}{2} = C$$
$$y = D$$

which gives:

$$x = \frac{2C - D}{3}$$
$$y = D$$
$$z = A - \frac{2C + 2D}{3}$$

As another example may be taken a mixture of hydrogen, carbonic oxide, and hydride of ethyl or methyl gas; then, if x, y, and z represent the quantities of these gases present:

$$x = \frac{3A + 2C - 4D}{6}$$
$$y = \frac{3A - 2C + D}{3}$$
$$z = \frac{2C + 2D - 3A}{6}$$

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* The Table is taken from the Handwörterbuch der Chemie.

(For further details, see Bunsen's Gasometry, translated by Roscoe, London, 1857, pp. 42—114; Regnault, "Cours élémentaire de chimie, Paris, 2^me^ éd. iv. 73—103; Handw. d. Chem. 2^te^ Aufl. i. 930—978.) W. J. R.

ANALYSIS, ZOOCHEMICAL. See ANALYSIS, ORGANIC, p. 250.

ANAMIRTIN, $C^{19}H^{36}O^2$.—The fatty matter extracted from grains of paradise or cocculus indicus (*Anamirta cocculus*), is composed of a solid glyceride, called *anamirtin* or *stearophanin*, together with a certain quantity of a free fatty acid. The seeds are first freed from picrotoxine and colouring matter by digestion in ether, then exhausted with hot ether, and the filtered ethereal solution is exposed to a low temperature. Anamirtin then separates in arborescent crystals, which are purified by two or three crystallisations from boiling absolute alcohol. It melts at 35 or 36° C., and on cooling solidifies in a wrinkled mass, but does not crystallise. It is waxy and not friable. (Francis, Ann. Ch. Pharm. xlii. 254.)

Anamirtic acid is obtained by saponifying anamirtin with caustic potash and decomposing the soap with hydrochloric acid. It then separates as a colourless oil which gradually solidifies in a white crystalline mass. When dissolved in boiling dilute alcohol, it crystallises on cooling in small needles, which have a nacreous lustre when dry. It melts at 68° C. and solidifies on cooling in very brilliant radiating masses. According to Francis (Ann. Ch. Pharm. xlii. 254) it contains $C^{35}H^{35}O^4$. Heintz, however (Lehrb. d. Zoochemie, pp. 387, and 1671), considers it to be identical with stearic acid. The *sodium-salt* separates from boiling absolute alcohol in elongated prisms. The *silver-salt* is a white precipitate, soluble in ammonia, and soon blackened by exposure to light. *Anamirtate of ethyl* is obtained by passing hydrochloric acid gas for several hours into a hot alcoholic solution of anamirtic acid. It separates at the surface of the liquid, in the form of a nearly colourless oil, which solidifies on cooling. It is but slightly volatile, and is partly decomposed by distillation. It contains 76·4 per cent. of carbon, and 12·69 of oxygen.

ANANAS, OIL OR ESSENCE OF. A solution of butyrate of ethyl in 8 or 10 times its weight of alcohol possesses the odour of the pine-apple (*Ananassa sativa*), and is employed in confectionery and perfumery, also to imitate the flavour of rum. The butyrate of ethyl thus used must be quite free from volatile fatty acids. (Hofmann Ann. Ch. Pharm. lxxxi. 87.)

ANATASE. *Octahedrite. Titane anatase.* TiO^2.—A pure or nearly pure oxide of titanium crystallised in octahedrons, belonging to the quadratic or dimetric system, with angles of terminal edges, = 136°22 and of lateral edges 97°56. The crystals are often very much elongated: hence the name, from ἀνάτασις, erection. The mineral has an adamantine lustre, exhibiting various degrees of translucency down to complete opacity; its colour by transmitted light is greenish-yellow; by reflected light yellow-grey, honey-yellow, hyacinth-red, clove-brown, and iron-black, more rarely dark sky-blue or indigo. Cleavage distinct parallel to the octahedral faces. Specific gravity 3·83—3·95, sometimes after heating, 4·11—4·16. Hardness 5·5—6. It is brittle, with sub-conchoïdal fracture, and yields a colourless powder. Streak uncoloured. Infusible before the blow-pipe. Anatase is found most abundantly at Bourg d'Oisans, in Dauphiné, with felspar, axinite, and ilmenite. It occurs with mica slate in the Grisons; in Bavaria near Hof; in the Fichtelgebirg, Norway; and in the Urals; in chlorite in Devonshire; with Brookite at Tremadoc, North Wales; in Brazil, in quartz, and in highly lustrous detached crystals. It is also said to occur in the slags from the iron furnaces of Orange County, New York. (Dana ii. 122; Handw. d. Chem. 2^te^. Aufl. i. 990). (See BROOKITE, RUTILE, TITANIC ACID.)

ANATTA. See ANNOTTO.

ANAUXITE. The name given by Breithaupt to a hydrated silicate of magnesium and aluminium found at Bilin in Bohemia. Its composition has not yet been ascertained with accuracy, but it contains 11·5 per cent. water, and 55·7 per cent. silica. It is softer than calc-spar, of a greenish-white colour, with mother-of-pearl lustre, translucent at the edges. Specific gravity 2·26. Cleavage in one direction very distinct. A doubtful species. (Handw. d. Chem. 2^te^ Aufl. i. 991.)

ANCHOIC ACID. $C^9H^{16}O^4 = C^9H^{14}O^2.H^2.O^2$. *Lepargylic acid.*—Discovered by Buckton (Chem. Soc. Qu. J. x. 166) among the products of the oxidation of Chinese wax by nitric acid; and by Wirz (Ann. Ch. Pharm. civ. 265) among the products of the action of nitric acid on the solid fatty acids of cocoa-nut oil.

Preparation.—1. When Chinese wax is heated for several hours with 4 or 5 times its volume of nitric acid, of specific gravity 1·39, the acid which distils over being continually poured back, a greenish distillate is obtained, containing caprylic, œnanthylic, and butyric acids, and a residue consisting of anchoic acid, together with suberic and pimelic acids. On boiling this residue with water, evaporating the filtrate to the crystallising point, pressing the crystalline crusts thus obtained, washing with ether, and recrystallising from hot water, anchoic acid crystallises out pure, the other acid remaining in solution. Cerotic acid also yields anchoic acid when treated with nitric acid, but not so readily as Chinese wax (Buckton).—2. Several pounds of the solid fatty acids of cocoa-nut oil (obtained by decomposing the soda soap with dilute sulphuric acid, and distilling off the volatile acid), are digested with nitric acid for several weeks till the oxidation is complete, and the mass solidifies in a white crystalline magma; this product is dissolved in twice its volume of hot water; and the granular mixture of suberic and anchoic acids which separates is redissolved and recrystallised several times, at last from weak alcohol, till the portion which first crystallises out exhibits the composition of pure anchoic acid. The mother-liquor separated from the crystalline magma of suberic and anchoic acids, contains several other acids of the series $C^nH^{2n-2}O^4$ (see ACIDS, p. 52) viz. pimelic, adipic, lipic, and succinic acid. (Wirz.)

Properties.—Anchoic acid forms snow-white aggregated nodules (Buckton); round granules resembling those of suberic acid, but harder (Wirz). Melts between 114° and 116° C. (Buckton); partially at 115°, completely at 124°, and solidifies on cooling, in a finely radiated nacreous mass (Wirz). At a stronger heat, it sublimes with partial decomposition, emitting white inodorous vapours, which produce a very suffocating effect when inhaled (Buckton): hence the name (ἄγχειν, to suffocate). It dissolves in 217·4 pts. of water at 18° C. and volatalises partially when the solution is evaporated (Wirz). Hot water dissolves it readily, the solution becoming whiter and semi-fluid on cooling (Buckton). It dissolves also in alcohol; has an acid taste and reaction.

Anchoic acid is dibasic, the formula of the neutral anchoates being $C^9H^{14}O^2.M^2.O^2$. It also forms acid salts. *Anchoate of ammonium* is an amorphous mass, which dissolves readily in water and alcohol, and gives off ammonia when heated. *Neutral anchoate of potassium* forms indistinct crystalline masses, which dissolve readily in water. The *acid* salt, $C^9H^{15}KO^4$, forms microscopic granules, which remain unaltered at 140° C. It dissolves in 3 pts. of cold water, more readily in hot water; soluble also in wood-spirit (Buckton). The *sodium*-salt crystallises more readily than the potassium-salt. *Neutral anchoate of barium*, $C^9H^{14}Ba^2O^4$, is obtained by neutralising the acid with baryta-water, or with carbonate of barium, or by precipitating a mixture of the ammonium-salt and chloride of barium with alcohol. Forms a transparent film which becomes dull at 100° C. (Buckton). After drying over sulphuric acid, it forms a white opaque mass, having the aspect of porcelain (Wirz). It is very soluble in water, insoluble in alcohol and in ether (Buckton). It does not appear possible to prepare an acid anchoate of barium (Buckton).

The ammonium-salt forms a gelatinous precipitate with chloride of *calcium*, white with acetate of *lead*, whitish with *ferrous* sulphate, light brick-red with *ferric* chloride, and bluish-green with *cupric* sulphate (Wirz). It also precipitates *zinc*-salts, *mercurous* salts and *mercuric* salts (Buckton.) *Anchoate of silver* $C^9H^{14}Ag^2O^4$, obtained by precipitation from the ammonium-salt, forms a white powder which soon decomposes when moist (Wirz): white flocks, which are permanent at 120° C., and dissolve sparingly in water. (Buckton.)

Anchoate of Ethyl. $C^{13}H^{24}O^4 = C^9H^{14}O^4.(C^2H^5)^2$.—Obtained by passing hydrochloric acid gas into the alcoholic solution of the acid. It is a yellowish viscid oil, lighter than water and having an agreeable odour. It boils at 325° C. (Buckton). Becomes brown without distilling at 260° (Wirz).

ANCHUSIN, or **ANCHUSIC ACID.** The colouring principle of the alkanet root (*Anchusa tinctoria*). It is extracted by first macerating the root in cold water, to extract the matters soluble in that liquid, then drying it in a stove, and exhausting with alcohol. The solution, at first red, becomes violet by boiling, then of a greyish-green; these changes of colour may, however, be prevented by adding a few drops of hydrochloric acid. The extract is concentrated, and agitated with ether, which then becomes charged with the colouring matter, and yields it by evaporation in the form of a resinous mass. Anchusin is an amorphous substance, having a deep red colour and resinous fracture: the colour is not altered by exposure to light. It softens at 60° C. At a higher temperature, it gives off very pungent violet vapours, similar to those of iodine; at a very high temperature, it becomes carbonised. It is insoluble in water, but dissolves in alcohol, and especially in ether; oil of turpentine, and fixed oils also dissolve it. According to Bolley and Wydler (Ann. Ch. Pharm. lii. 141) it contains $C^{35}H^{40}O^8$; 71·33 p. c. C; 7·00 H.

Nitric acid transforms anchusin into oxalic acid and a bitter substance. Concentrated sulphuric acid dissolves it, forming a solution of a beautiful amethyst colour.

The alkalis form with anchusin blue compounds, soluble in water, less soluble in alcohol and ether. With subacetate of lead it forms a bluish-grey precipitate soluble in alcohol.

The alcoholic solution of anchusin evaporated over the water-bath, leaves a blackish green residue from which water extracts a brown substance. The insoluble portion well washed with water and then treated with ether, yields a green extract containing, according to Bolley and Wydler, $C^{34}H^{44}O^{8}$, and formed from anchusin by fixation of water, and elimination of carbonic anhydride;

$$C^{35}H^{40}O^{8} + 2H^{2}O = C^{34}H^{44}O^{8} + CO^{2}.$$

ANDALUSITE. $Al^{4}O^{3}.SiO^{2}$, or $3Al^{2}O^{3}.2SiO^{3}$.—A crystallised mineral, found originally in the Spanish province of Andalusia, and occurring also in Scotland, Ireland the Pyrenees, and other localities, in mica-slate, and others of the older rocks. It forms rhombic prisms, belonging to the trimetric system, with angles of 91° 35′, and 88° 27′. Specific gravity from 3·0 to 3·2. Hardness = 7·5. It is infusible before the blowpipe: dissolves with difficulty in borax, forming a clear glass, and even less easily in phosphorus salt. It is insoluble in acids. The alumina is generally more or less replaced by the sesquioxide of iron and manganese. The minerals *chiastolite* and *cyanite* have the same composition as andalusite: cyanite, however, belongs to the triclinic (doubly oblique prismatic) system, and is found in the oldest plutonic rocks, whereas andalusite and cyanite occur in metamorphic rocks, as in mica-slate and clay-slate. Crystals are also found having the external form of andalusite, but made up of a mass of fine crystalline grains of cyanite. (Handw. d. Chem. 2te Aufl. i. 991; Gm. iii. 412; Dana, ii. 257.)

ANDAQUIES-WAX. (*Cera de los Andaquies.*)—The wax of a peculiar species of bee, found near the Oronoco and Amazon rivers, and used as a substitute for ordinary beeswax, in the manufacture of candles, &c. According to Lewy (Ann. Ch. Phys. [3] xiii. 458), it has a density of 0·917, melts at 77° C., and contains 81·6 per cent. C, 13·5 H, and 4·8 O. It is not, however, a definite compound, but, like ordinary beeswax, is a mixture of three different fats, one of which, constituting about half the entire substance, is insoluble in alcohol, melts at 72° C., and is identical with palm-wax. The solution obtained by boiling the original wax with alcohol deposits on cooling, a fat which melts at 82° C., and agrees in every respect with *cerosin* obtained from the sugar-cane; this substance exists in the Andaquies-wax to the amount of 45 per cent. Lastly, the alcoholic mother-liquor yields by evaporation about 5 per cent. of an oily fat, not yet further examined.

ANDESIN. A mineral resembling felspar in external appearance, but differing from it essentially in composition. It may be represented by the general formula $\left.\begin{matrix}M^{2}\\Al^{4}\end{matrix}\right\}4SiO^{3} = M^{2}O.SiO^{3} + Al^{4}O^{3}.3SiO^{3}$, or (regarding silicic acid as tribasic) = $3MO.2SiO^{3} + 3(Al^{2}O^{3}.2SiO^{3})$, the symbol M denoting potassium, sodium, calcium, or magnesium, which metals may replace each other in any proportions. Specific gravity 2·733. The mineral was originally obtained from the Andes, but has since been found in the Vosges and in other localities. (Handw. d. Chem. 2te Aufl. i. 993.)

ANDREASBERGOLITE and **ANDREOLITE.** See HARMOTOME.

ANEMONIN. $C^{15}H^{12}O^{6}$ (?)—A crystalline body, obtained from the leaves of several species of anemone, viz. *Anemone pulsatilla*, *A. pratensis*, and *A. nemorosa*. Water distilled off these leaves deposits, after some weeks, a white inodorous substance, which softens at 150° C., giving off water and acrid vapours. It is purified by repeated recrystallisation from boiling alcohol.

The crystals belong to the trimetric system. In the cold, they are but sparingly soluble in alcohol; ether and water dissolve but little, even at a boiling heat; the solutions are neutral. Anemonin is a poisonous substance; applied to the skin, it produces slight irritation.

By the action of alkalis, anemonin is transformed into anemonic acid. Boiled with water and oxide of lead, it yields a crystalline compound, $C^{15}H^{12}O^{11}.PbO$, soluble in boiling water. Strong sulphuric acid blackens anemonin. Hydrochloric acid dissolves it without sensible alteration. By oxidising agents, such as peroxide of manganese and sulphuric acid, it is converted into formic acid. Chlorine attacks it readily when heated, forming hydrochloric acid and an oily volatile body.

Anemonic Acid.—This name has been applied to an acid substance produced by the action of baryta-water on anemonin (Löwig and Weidmann, Pogg. Ann. xlvi. 45), and likewise to an amorphous substance, which is deposited together with anemonin, from distilled anemone water (Schwarz, Mag. Pharm. x. 193; xix. 168;

Fehling, Ann. Ch. Pharm. xxxviii. 218). Both these substances are said to consist of anemonin together with the elements of water. (Gerhardt, Traité iv. 263.)

ANGELICA BALSAM. When the root of archangel (*Angelica archangelica*) is exhausted with strong alcohol, and the residue left after distilling off the greater part of the alcohol is evaporated over the water-bath, a viscid mass is obtained, which, when washed with water and digested in ether, yields a solution from which, by evaporation, a black-brown balsam is obtained, amounting to about 6 per cent. of the root. This balsam is a mixed product, and on treating it with potash-ley and distilling off part of the water, a small quantity of an essential oil (*angelica-oil*) separates; on continuing to heat the mass with the alkaline liquid, a waxy body (*angelica-wax*), is left behind: and the liquid concentrated to a certain point yields a crystalline resin, *angelicin*. On distilling the residue with excess of sulphuric acid, butyric acid passes over with the water, and afterwards angelic acid. (Buchner, Ann. Ch. Pharm. xlii. 226.)

ANGELIC ACID. $C^5H^8O^2 = \left.\begin{matrix}C^5H^7O\\H\end{matrix}\right\}O$, [or $C^{10}H^7O^3.HO.$]—This acid exists in the root of the archangel, *Angelica archangelica* (Buchner, Ann. Ch. Pharm. xlii. 226), and in sumbul, or moschus root, a drug imported from Asia Minor, and probably also belonging to an umbelliferous plant. From *archangel root* it is prepared by boiling fifty pounds of the root, cut into small pieces, with four pounds of lime and with water, straining through a cloth, concentrating the liquid, and distilling it with dilute sulphuric acid. A complex distillate is then obtained, which is neutralised with potash, and evaporated to dryness over the water-bath. The residue, distilled with sulphuric acid diluted with twice its weight of water, yields first a distillate of water, acetic acid, and valerianic acid, and afterwards angelic acid, part of which crystallises in the neck of the retort, while the rest passes into the receiver; on leaving the distilled liquid in a cold place for some days, the angelic acid dissolved in it crystallises out. The crystals are washed with a small quantity of water, and repeatedly crystallised to free them from valerianic acid (Meyer and Zenner, Ann. Ch. Pharm. lv. 307).—From *sumbul root* the acid is obtained by exhausting the root with alcohol, evaporating the filtered solution, boiling the residual balsam with strong potash-solution, filtering to separate a volatile oil, mixing the brown-red alkaline filtrate with sulphuric acid, which separates a dark brown oil, and distilling this oil with water, added at intervals as long as the distillate continues to be mixed with drops of oil. This distillate, set aside in a cold place, deposits angelic acid, which may be purified by twice saturating it with carbonate of sodium, distilling with sulphuric acid, then distilling it alone, and lastly, boiling it for a long time to separate sumbulamic acid. (Reinsch, Jahrb. pr. Pharm. vii. 79.)

Angelic acid is also produced by heating the essential oil of chamomile (*Anthemis nobilis*)—which consists of angelic aldehyde, together with a hydrocarbon (C^5H^8)—with hydrate of potassium:

$$\underset{\substack{\text{Angelic}\\\text{aldehyde.}}}{C^5H^8O} + KHO = \underset{\substack{\text{Angelate of}\\\text{potassium.}}}{C^5H^7KO^2} + 2H$$

The oil must be gently heated with pulverised and tolerably dry potash, till the temperature of the mass rises considerably, and hydrogen begins to escape. If the source of heat be then removed, the action goes on by itself, the hydrocarbon volatilises, and angelate of potassium remains mixed with the excess of hydrate. On dissolving this residue in water, taking off the small remaining portion of oily hydrocarbon with a pipette, and treating the solution with sulphuric acid, angelic acid rises to the surface in the form of an oil, which solidifies in a crystalline mass on cooling. This mode of preparation is much more productive than the preceding, provided the application of heat be discontinued at the right time. If it be continued too long, with the view of expelling the whole of the hydrocarbon not attacked by the potash, a considerable portion of the angelic acid will be resolved into acetic and propionic acids:

$$C^5H^8O^2 + 2H^2O = C^2H^4O^2 + C^3H^6O^2 + H^2,$$

the admixture of which greatly impedes the crystallisation of the angelic acid. (Gerhardt, Traité ii. 449.)

Angelic acid is also produced, together with oreoselin, by treating peucedanin with alcoholic potash:

$$\underset{\substack{\text{Peuce-}\\\text{danin.}}}{C^{12}H^{12}O^3} + KHO = \underset{\substack{\text{Angelate}\\\text{of potassium.}}}{C^5H^7KO^2} + \underset{\text{Oreoselin.}}{C^7H^6O^2}$$

(Wagner, J. pr. Chem. lxii. 275.)

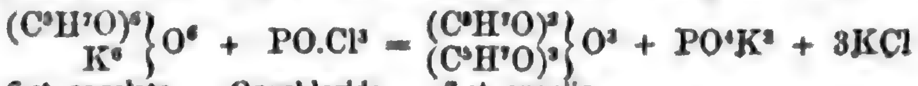
Angelic acid crystallises in large long prisms and needles, which are colourless and transparent. It melts at 45° C., boils at 190°, and distils without decomposition. It has a peculiar aromatic odour, a sour but aromatic taste, and reddens litmus. It burns with a bright and rather smoky flame. It dissolves sparingly in cold, but abundantly in hot water, whence it crystallises in needles on cooling. In alcohol, ether, oil of turpentine, and fat oils, it dissolves with great facility.

Angelic acid is monobasic, and belongs to the series of acids whose general formula is $\left.\begin{matrix} C^nH^{2n-3}O \\ H \end{matrix}\right\} O$, the other known members of which are acrylic acid (C^3), pyroterebic (C^6), hypogæic (C^{16}), and oleic (C^{18}).

The angelates of the *alkali-metals* are soluble in water and alcohol. The *calcium*-salt, $C^5H^7CaO^2 + H^2O$, forms shining laminæ, very soluble in water. The soluble angelates form with *lead*-salts, a white precipitate, $C^5H^7PbO^2$, soluble in a large quantity of water; with *ferric* salts, a flesh-coloured insoluble precipitate; with *cupric* salts, a bluish-white sparingly soluble precipitate; with *mercurous* nitrate, a white precipitate, which soon turns grey and redissolves; with *mercuric* chloride, no precipitate; and with nitrate of *silver*, a white precipitate, which dissolves in a large quantity of water, forming a solution which after a while deposits metallic silver.—A somewhat acid solution of oxide of silver in the boiling aqueous acid, yields, when evaporated at the gentlest possible heat, small greyish-white crystals of the normal silver-salt, $C^5H^7AgO^2$, sometimes also laminæ of a basic salt. (Meyer and Zenner.)

Angelate of Ethyl, Angelic Ether, is obtained by distilling angelate of sodium with a mixture of 1 pt. strong sulphuric acid, and 2 pts. of 94 per cent. alcohol. It is a colourless oily liquid, which smells like sour apples, has a sweetish, burning, aromatic taste, and excites coughing and headache when inhaled. (Reinsch and Recker, Jahrb. pr. Pharm. xvi. 12.)

ANGELIC ANHYDRIDE, or *Anhydrous Angelic Acid*, $C^{10}H^{14}O^3 = (C^5H^7O)^2O$.—Produced by the action of oxychloride of phosphorus on angelate of potassium:



$$\left.\begin{matrix}(C^5H^7O)^6 \\ K^6\end{matrix}\right\} O^6 + PO.Cl^3 = \left.\begin{matrix}(C^5H^7O)^3 \\ (C^5H^7O)^3\end{matrix}\right\} O^3 + PO^4K^3 + 3KCl$$

6 at. angelate of potassium. Oxychloride of phosphorus. 3 at. angelic anhydride.

The viscid oil resulting from the action yields, when treated with carbonate of sodium and then with ether, a solution which leaves the anhydride on evaporation. It is a perfectly neutral, limpid oil, heavier than water, and having a peculiar odour quite different from that of angelic acid. It does not crystallise, even at the temperature of a mixture of ice and salt. When distilled, it begins to boil at 240° C., but the boiling-point soon rises to 250°, and the compound is subsequently decomposed, yielding a distillate of angelic acid and a neutral oil, and leaving a carbonaceous residue.—The anhydride is but slowly rendered acid by the action of water, but dissolves readily in strong alkaline liquids. Aqueous ammonia first converts it into a buttery mass, and then dissolves it. In contact with aniline, it becomes strongly heated, and deposits crystals of *phenyl-angelamide*, $N.H,C^6H^5,C^5H^7O$. (Chiozza, Ann. Ch. Phys. [3] xxxix. 210.)

ANGELICIN. A crystalline substance obtained, according to Buchner, by treating angelica-balsam with potash (p. 287).

ANGLARITE. A variety of vivianite, found at Arglac, in the department of the Haute-Vienne, France.

ANGLESITE. Native Sulphate of Lead.

ANGUSTURINE. An organic base, said by Brande to exist in true angustura bark, *Cusparia febrifuga*. Its existence is doubtful.

ANHYDRIDES. *Secondary Negative Oxides*, or *Oxides of Acid-radicles*.—These bodies are also often called *anhydrous acids*, and are sometimes even confounded with *acids*. As regards their composition, they stand in the same relation to acids as oxide of potassium, K^2O, to potash, KHO; or, generally, as anhydrous (secondary) oxides, to hydrates (primary oxides): that is, they represent one or more atoms of water, nH^2O (the substance taken as the standard of comparison for all oxides), in which the whole of the hydrogen is replaced by one or more negative radicles; while the corresponding acids represent one or more atoms of water in which the same radicles replace one half of the hydrogen.

For example:—

Hypochlorous	anhydride	$= Cl.Cl.O$,	hypochlorous	acid	$= H.Cl.O$,
Nitric	„	$= NO^2.NO^2.O$,	nitric	„	$= H.NO^2.O$,
Acetic	„	$= C^2H^3O.C^2H^3O.O$,	acetic	„	$= H.C^2H^3O.O$,
Benzoic	„	$= C^7H^5O.C^7H^5O.O$,	benzoic	„	$= H.C^7H^5O.O$,

Aceto-benzoic anhydride = $C^2H^3O.C^7H^5O.O$,
Sulphuric „ = $SO^2.O$, sulphuric acid = $H^2.SO^2.O^2$,
Succinic „ = $C^4H^4O^2.O$, succinic „ = $H^2.C^4H^4O^2.O^2$,
Phosphoric „ = $PO.PO.O^3$, phosphoric „ = $H^3.PO.O^3$.

From these instances it is evident that there are three classes of anhydrides, namely. (*a*) those which derive from 1 at. water by the replacement of H^2 by 2 atoms of the same monatomic acid-radicle (hypochlorous, acetic, &c.), or by 2 different monatomic radicles (aceto-benzoic, &c.); (*b*) those which derive from 1 at. water by the replacement of H^2 by 1 atom of a diatomic acid-radicle (sulphuric, &c.); (*c*) those which derive from 3 at. water by the replacement of H^6 by 2 atoms of a triatomic acid-radicle (phosphoric). Anhydrides deriving from 2 at. water have not yet been shown to exist.

All anhydrides are more or less quickly converted into acids by the action of water or of hydrates; in the dry state, or when dissolved in ether or other liquids which do not change them into acids, they are without action on litmus or other vegetable colours.

Anhydrides (*a*) are obtained by the action of chlorides of monatomic acid-radicles on monatomic acids or salts:

$$Cl.Cl + \underset{\text{Hypochlorite of mercury.}}{Hg.Cl.O} = Hg.Cl + \underset{\text{Hypochlorous anhydride.}}{Cl.Cl.O.}$$

$$\underset{\text{Chloride of benzoyl.}}{C^7H^5O.Cl} + \underset{\text{Acetate of potassium.}}{K.C^2H^3O.O} = KCl + \underset{\text{Aceto-benzoic anhydride}}{C^2H^3O.C^7H^5O.O.}$$

They are liquid, or solid bodies, and those which contain only one acid-radicle, are usually volatile without decomposition: those which contain two acid-radicles are decomposed by heat into two anhydrides, each containing one radicle.

$$\underset{\text{Aceto-benzoic anhydride.}}{C^2H^3O.C^7H^5O.O} + \underset{\text{Aceto-benzoic anhydride.}}{C^2H^3O.C^7H^5O.O} = \underset{\text{Acetic anhydride.}}{C^2H^3O.C^2H^3O.O} + \underset{\text{Benzoic anhydride.}}{C^7H^5O.C^7H^5O.O.}$$

The anhydrides of this class, which correspond to organic acids, are insoluble or but slightly soluble in water; they dissolve in alcohol, but are gradually decomposed by it forming salts of ethyl (compound ethers); in ether they dissolve without alteration.

Ammonia and its derivatives convert them into amides, or alkalamides.

$$\underset{\text{Benzoic anhydride.}}{C^7H^5O.C^7H^5O.O} + 2NH^3 = H^2O + \underset{\text{2 at. benzamide.}}{2(N.C^7H^5O.H^2)}$$

$$\underset{\text{Acetic anhydride.}}{C^2H^3O.C^2H^3O.O} + \underset{\text{2 at. phenylamine (aniline).}}{2N.C^6H^5.H^2} = H^2O + \underset{\text{2 at. phenylacetamide.}}{2(N.C^2H^3O.C^6H^5.H)}$$

With perchloride of phosphorus they give chlorides of monatomic acid-radicles: with sulphide of phosphorus, sulphanhydrides (secondary negative sulphides).

The anhydrides (*b*) correspond to dibasic or diatomic acids. They are formed by the decomposition of these acids, or their salts, by heat.

$$\underset{\text{Succinic acid.}}{H^2.C^4H^4O^2.O^2} = H^2O + \underset{\text{Succinic anhydride.}}{C^4H^4O^2.O}$$

$$\underset{\text{Sesquisulphate of iron.}}{Fe^4.(SO^2)^3.O^6} = \underset{\text{Sesquioxide of iron.}}{Fe^4O^3} + \underset{\text{3 at. sulphuric anhydride.}}{3(SO^2.O)}$$

With ammonia, they give ammonium-salts of amic acids:

$$\underset{\text{Succinic anhydride.}}{C^4H^4O^2.O} + 2NH^3 = \underset{\text{Succinamate of ammonium.}}{N.C^4H^4O^2.H^2NH^4.O}$$

and, to some extent, also secondary amides (imides):

$$\underset{\text{Succinic anhydride.}}{C^4H^4O^2.O} + NH^3 = H^2O + \underset{\text{Succinimide.}}{N.C^4H^4O^2.H}$$

They react in a similar way with phenylamine (aniline) and some other primary derivatives of ammonia.

Perchloride of phosphorus converts them into chlorides of diatomic acid-radicles.

In the case of sulphuric anhydride, SO^3, or $SO^2.O$, which has been much more minutely studied than any other anhydride of this class, certain additional reactions have been observed. For instance, it has been found to combine with hydrochloric acid, forming chlorhydro-sulphuric acid:

$$SO^3 + HCl = \underset{\text{Chlorhydro-sulphuric acid.}}{HSO^3Cl}$$

as well as with other chlorides, inorganic and organic (chlorides of ammonium, barium, ethyl, phenyl, &c.), to form compounds which represent the metallic salts and ethers of this acid. It also combines with hydrocarbons, producing neutral compounds of varying constitution:

$$2SO^3 + \underset{\text{Ethylene.}}{C^2H^4} = \underset{\text{Ethionic anhydride.}}{C^2H^4S^2O^6}$$

$$SO^3 + \underset{\text{2 at. benzine.}}{2C^6H^6} = H^2O + \underset{\text{Sulphobenzide.}}{C^{12}H^{10}SO^2}$$

The comparison of these reactions with those produced by acids in similar circumstances (see pp. 43, 44), makes it clearly evident that anhydrides and acids are essentially different in their chemical characters.

Very few triatomic anhydrides (*c*) are yet known. Phosphoric anhydride, P^2O^5, or $PO.PO.O^3$, is the only well known member of this class. It is obtained by the direct combination of phosphorus and oxygen. Ammonia converts it into phosphamic acid:

$$PO.PO.O^3 + 2NH^3 = H^2O + 2(NH.PO.HO)$$

with perchloride of phosphorus it gives oxychloride of phosphorus (chloride of phosphoryl); and, like sulphuric anhydride, it combines with hydrochloric acid.—G. C. F.

ANHYDRITE. Anhydrous sulphate of calcium. There are six varieties of it: 1. *Compact.* Has various shades of white, blue, and red; massive and kidney-shaped; dull aspect; splintery or conchoïdal fracture; translucent on the edges; is scratched by fluor, but scratches calc-spar; somewhat tough: specific gravity 2·850. It contains a trace of sea-salt. It is found in the salt mines of Austria and Salzburg, and at the foot of the Harz mountains; also in the gypsum pits at Ashton-on-Trent, near Derby. —2. *Granular.* The scaly of Jameson, is found in massive concretions, of which the structure is confusedly foliated. White or bluish colour, with a pearly lustre. Composition as above, with 1 per cent. of sea-salt. It occurs in the salt mines of Halle. Specific gravity 2·957. — 3. *Fibrous.* Massive; glimmering, pearly lustre; fracture in delicate parallel fibres; scarcely translucent; easily broken. Found at Halle, Ischel, and near Brunswick.—4. *Radiated.* Blue, sometimes spotted with red; radiated, splendent fracture; partly splintery; translucent; not hard; specific gravity 2·940.—5. *Sparry* or *Cube-spar.* Milk-white colour, passing sometimes into greyish and reddish-white; short four-sided prisms, belonging to the trimetric system, having two of the opposite sides much broader than the other two; occasionally the lateral edges are truncated, whence results an eight-sided prism belonging to the trimetric system; lustre splendent, pearly; foliated fracture; threefold rectangular cleavage; cubical fragments; translucent; scratches calc-spar; brittle; specific gravity 2·9. This is the *muriacite* of some writers. It is doubly refracting. It is said to contain 1 per cent. of sea-salt. It is found at Bex in Switzerland, and Halle in the Tyrol.—6. *Siliciferous,* or *Vulpinite.* Massive concretions of a laminated structure; translucent on the edges; splendent and brittle: greyish-white, veined with bluish-grey; specific gravity 2·88. It contains 8 per cent. silica; the rest is sulphate of calcium. It is called by statuaries, *Marmo bardiglio di Bergamo,* and takes a fine polish. It derives its name from Vulpino in Italy, where it accompanies lime. U.

ANIL. A nearly obsolete synonyme of indigo. The same term is also used as a synonyme of PHENYLIMIDE (*q. v.*)

ANILAMIC ACID. Syn. of PHENYLAMIC ACID.

ANILIDES. Syn. of PHENYLAMIDES.

ANILINE. Syn. of PHENYLAMINE.

ANIMALISATION. The process or series of processes by which food is converted into the constituents of the animal body (see DIGESTION and NUTRITION). The same term is used in the arts to denote the operation by which vegetable fibres, such as cotton and flax, are made to unite with albuminous substances.

ANIMÉ RESIN, improperly called *gum-animé.*—A resinous substance used for fumigation. There are three varieties of it, the East Indian, the West Indian, and the brown American. West Indian animé, sometimes called *courbaril resin*, is the produce of the *Hymenæa Courbaril*, a tree belonging to the order *Cæsalpineæ*, growing in the West Indies and in South America; the other varieties are of unknown origin. The West Indian resin forms yellowish-white transparent, somewhat unctuous tears, or sometimes larger masses; it is brittle; of a light pleasant taste, and very agreeable odour; hence its use in fumigation and in perfumery. It softens in the mouth, melts easily in the fire, and burns with a bright flame. Specific gravity 1·028 (Bresson), 1·032 (Paoli). Insoluble in water, perfectly soluble in hot alcohol. Cold alcohol dissolves about 54 per cent. of it. The soluble portion is, according to Laurent, identical with the resin of turpentine. The insoluble portion crystallises from boiling alcohol in slender colourless needles, consisting, according to Laurent, of 83·6 per cent. C, 11·5 H, and 4·9 O, agreeing with the formula $C^{22}H^{36}O$. According to Filhol, the resin of *Hymenæa Courbaril* is nearly insoluble in cold absolute alcohol, melts at 100° C, and contains 85·3 per cent. carbon, 11·5 hydrogen, and 3·2 oxygen.

Brown American animé softens in the mouth, and dissolves completely in cold alcohol; specific gravity 1·0781 (Paoli). Oriental animé, which, according to Guiboust, is no longer met with in commerce, is likewise perfectly soluble in cold alcohol, has a density of 1·027, and appears to consist of two resins, differing in melting point (Paoli, Trommsdorff's Journ. Bd. ix. St. 1; s. 40, 61; Guiboust, Rev. Scient. xvi. 177; Laurent, Ann. Ch. Phys. [2] lxvi. 315; Gerhardt, Traité, iii. 669; Filhol, J. Pharm. [3] i. 301, 507.)

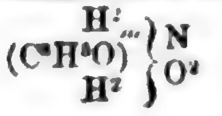
There is some confusion respecting the use of the word *animé*, the French designating copal as *résine animé;* and denoting the West Indian animé or courbaril resin, by the term *Copal* or *animé tendre*.

ANIMINE. An organic base obtained, together with three others, *odorine*, *ammoline*, and *olanine*, from bone-oil (*Oleum animale Dippelii*), by Unverdorben in 1826 (Pogg. Ann. xi. 59 and 67). None of these bases were prepared by Unverdorben in a state of purity. Odorine was afterwards obtained pure, and more exactly investigated under the name of *picoline*, by Anderson, who showed that it is isomeric with aniline, C^6H^7N. The other three bases, which were less volatile than odorine, were probably mixtures of the homologous bases *lutidine*, C^7H^9N, and *collidine*, $C^8H^{11}N$, together with other substances. (See Gm. xi. 273.)

ANION (from ἄνιον, that which goes up).—A term used by Faraday to denote the element of an electrolyte, which is eliminated at the positive pole or *anode;* the other element, which is eliminated at the negative pole or *kathode*, being called a *kation* (κατιον, that which goes down). To understand these terms, we must suppose the decomposing body to be so placed that the current (of positive electricity) passing through it, shall be parallel to, and in the same direction with, that which is supposed to exist in the earth, viz. from east to west, or in the direction of the sun's diurnal motion. The positive pole or electrode will then be towards the east. (Faraday's Experimental Researches in Electricity, vol i. p. 196.)

ANISAMIC ACID. $C^8H^9NO^3$. (Zinin, Ann. Ch. Pharm. xcii. 327.) — Obtained by passing hydrosulphuric acid into a mixture of nitranisic acid with 8 pts. of alcoholic ammonia. After twelve hours, when the acid is dissolved, the whole is boiled, with occasional addition of water, till all the alcohol is driven off; it is then filtered from the separated sulphur, and mixed with acetic acid, which precipitates anisamic acid in long brown needles: they are obtained colourless by solution in water and treatment with animal charcoal. It forms thin, brilliant, four-sided prisms, which dissolve but slightly even in boiling water, or in ether, but are readily soluble in alcohol. Hydrochloric and boiling acetic acid dissolve it unchanged; its solution in dilute nitric acid reddens on long boiling, and by cooling deposits brown flakes and a white pulverulent substance. It melts at 180°C., and is decomposed at a higher temperature.—The only anisamate that has been analysed is the *silver-salt*, $C^8H^8AgNO^3$: it is a curdy precipitate, insoluble in water, readily soluble in ammonia and acids; in the dry state, it may be heated to 120° C. without decomposition, but turns brown when boiled with water. The *ammonium-salt* is very soluble, and crystallises with difficulty in four-sided tables; its aqueous solution is partially decomposed by boiling, ammonia being evolved, and the acid crystallising out on cooling. The *lead* and *cadmium-salts* are white precipitates. An aqueous solution of anisamic acid does not precipitate lime- or baryta-water, or silver-salts. With ammoniacal sulphate of copper, it gives, in the cold, a light blue flocculent precipitate, which, on boiling, becomes pulverulent, and of a cinnamon colour.

The mode of formation of anisamic from anisic acid being analogous to that of oxybenzamic acid from benzoic acid, it should perhaps be regarded as *oxyanisamic acid*,



$$\left.\begin{matrix}H' \\ (C^8H^6O)''' \\ H^2\end{matrix}\right\}\begin{matrix}N \\ O^2\end{matrix}$$

F. T. C.

ANISAMIDE. $C^8H^9NO^2$ [or, rather, *anisamic acid*, $\left.\begin{matrix}H^2\\(C^8H^6O)''\\H\end{matrix}\right\}\begin{matrix}N\\O\end{matrix}$]. (Cahours, Ann. Ch. Phys. [3] xxii. 353.)—Obtained by treating chloride of anisyl with dry ammonia, whereupon heat is evolved, and the mixture becomes a solid mass of anisamide, which is soluble in alcohol, whence it crystallises by spontaneous evaporation in large prisms. It is also formed by the action of ammonia on anisate of ethyl in a closed vessel. F. T. C.

ANISAMINES (Cannizzaro, Compt. rend. l. 1100).—These bases are produced by the action of strong alcoholic ammonia on the chlorhydrin of anisic alcohol (C^8H^9OCl):

$$C^8H^9OCl + NH^3 = \underset{\text{Anisamine.}}{C^8H^{11}ON} + HCl.$$

$$2C^8H^9OCl + NH^3 = \underset{\text{Dianisamine.}}{C^{16}H^{19}O^2N} + 2HCl.$$

The resulting mass is freed from sal-ammoniac by digestion in water, then dissolved in alcohol, and the residue obtained by evaporating the alcoholic solution to dryness, consists, after washing with ether, of a mixture of the hydrochlorates of the two bases. These hydrochlorates are separated by water, the anisamine-salt being much the more soluble of the two; and the bases are obtained in the free state by adding ammonia or potash to the solutions of the hydrochlorates, then agitating with ether, and evaporating the ethereal solution.

Anisamine crystallises in small needles, soluble in water, alcohol, and ether, and melting with colouration above 100° C. *Dianisamine* forms at first a thick oil, which, after a few days, crystallises in white laminæ. It is soluble in alcohol and in ether; less soluble in water than anisamine. It melts and solidifies between 32° and 33° C.

Both these alkaloids are strong bases. The *chloroplatinate of anisamine*, $C^8H^{11}ON.HCl.PtCl^2$, crystallises in small gold-yellow laminæ. The *chloroplatinate of dianisamine*, $C^{16}H^{19}O^2N,HCl.PtCl^2 + H^2O$ is precipitated as a brown oily liquid, gradually changing to a mass of yellow needles.

The constitution of these bases may be viewed in two different ways. If anisic alcohol be regarded as monatomic $= C^8H^9O.H.O$, the bases then appear as ordinary amines, containing the radicle C^8H^9O, viz.:

$$\text{Anisamine} = N\left\{\begin{matrix}H^2\\C^8H^9O\end{matrix}\right. ;\ \text{Dianisamine} = N\left\{\begin{matrix}H\\(C^8H^9O)^2\end{matrix}\right.$$

but if we suppose anisic alcohol to be diatomic $= (C^8H^8)''.H^2.O^2$, then the bases must be regarded as hydoramines (p. 197), viz.:

$$\text{Anisamine} = \begin{matrix}N\\O\end{matrix}\left\{\begin{matrix}(C^8H^8)''\\H^3\end{matrix}\right. ;\ \text{Dianisamine} = \begin{matrix}N\\O^2\end{matrix}\left\{\begin{matrix}(C^8\overset{''}{H^8})^2\\H^3\end{matrix}\right.$$

ANISANILIDE. See PHENYLANISAMIDE, under PHENYLAMINE.

ANISE, OIL OF. *Essence d'anis. Anisöl.*—The name given to the essential oil which is obtained by distillation with water from the seeds of the common anise (*Pimpinella anisum*), and the China or star anise (*Illicium anisatum*). (According to Hees, 20 lb. of seeds yield 5½ oz. oil.) This oil contains an oxygenated principle, which, by the action of oxidising agents, is converted into hydride of anisyl. The same principle is found in the oils extracted from fennel (*Anethum fœniculum*), and tarragon (*Artemisia Dracunculus*). All these oils may, therefore, be conveniently described in the same article, though they differ slightly in their physical properties.

1. *Oil of anise and of fennel* is a neutral, yellowish, somewhat syrupy liquid, possessing a peculiar aromatic smell and taste. Its specific gravity varies from 0·977 to 0·991. It is soluble in all proportions in cold alcohol of specific gravity 0·806, and in 2·4 pts. alcohol of specific gravity 0·84 at 25° C. It appears to consist of two distinct oils, one of which solidifies at temperatures below 10°, while the other remains fluid at all temperatures. Scarcely anything is known of the latter of these oils; according to Gerhardt (Traité, iii. 352 *et seq.*) it is isomeric with oil of turpentine. The former, which is generally known as *anethol* or *anise-camphor*, has been examined by Cahours (Ann. Ch. Phys. [3] iii. 274). The proportion of these two constituents varies in different specimens of the commercial oil; but generally the camphor composes ¾ of the whole. The crude oil absorbs oxygen when exposed to the air, becomes more syrupy, and finally loses the property of solidifying by cold. In order to obtain the camphor in a state of purity, it is freed from the liquid oil by pressure between folds of filtering paper, and repeatedly crystallised from alcohol of specific gravity 0·85. It crystallises in soft, white, lustrous laminæ, of specific gravity 1·014, having a smell similar to, but weaker and more agreeable than, that of the crude oil. It is very

friable, especially at 0° C.; melts at 18° C., and at 222° boils and volatilises completely, but not without slight coloration. Its formula is $C^{10}H^{12}O$. Its vapour-density. taken at 338° C., is 5·19; at lower temperatures, its density is higher. It is not affected by exposure to the air in the solid state; but, if kept in a state of fusion, it gradually ceases to solidify on cooling, and finally resinifies completely. *Nitric acid* converts it into hydride of anisyl, anisic or nitranisic acid, and oxalic acid; the products vary with the concentration of the acid. Generally a yellow resinous substance is also formed, to which Cahours gives the name *nitraniside*, and the formula $C^{10}H^{10}(NO^2)^2O$ (?). This is a very insoluble substance, which melts at about 100° C., and is completely decomposed by distillation; when treated with a strong solution of potash, it gives off ammonia abundantly, and is converted into a black substance, which Cahours calls *melanisic acid*. Under certain circumstances, the action of dilute nitric acid produces an acid containing 10 atoms carbon (see ANISOIC ACID). When distilled with *sulphuric acid* and *bichromate of potassium*, oil of anise yields anisic and acetic acids. (Hempel, Ann. Ch. Pharm. lix. 104.)

Strong boiling solutions of *caustic alkalis* do not attack oil of anise; but when it is heated with potash-lime in a sealed tube to the boiling point of the oil, a peculiar acid is formed, which appears to be isomeric with cuminic acid. (Gerhardt.)

Anise-camphor treated with *acid sulphite of sodium*, is resolved into methyl and hydride of anisyl, $C^{10}H^{12}O + H^2O = 2CH^3 + C^8H^8O^2$. (Städeler and Wächter Ann. Ch. Pharm. cxvi. 172.)

Anise-camphor absorbs *hydrochloric acid* gas abundantly, forming a liquid compound, $C^{10}H^{12}O.HCl$, which contains 19·8 per cent. chlorine. It absorbs *chlorine* rapidly, with evolution of heat and vapours of hydrochloric acid, forming substitution-products, in which the number of atoms of hydrogen replaced by chlorine varies with the duration of the action of the gas. The trichlorinated compound (*chloranisal*) $C^{10}H^9Cl^3O$, is a syrupy liquid, which is completely decomposed by distillation, and from which, by the further action of chlorine, aided by heat, a still higher chlorine compound may be obtained. Oil of anise treated with *pentachloride of phosphorus*, yields a liquid boiling at a high temperature, probably $C^{10}H^{12}Cl^2$. (Aelsmann and Kraut, J. pr. Chem. lxxvii. 490.)

When anhydrous *bromine* is gradually added to anise-camphor, heat and hydrobromic acid are evolved, and the whole becomes liquid, and finally, when the bromine is in excess, solidifies after a time; it is then washed with cold ether, and recrystallised from boiling ether. The *bromanisal*, $C^{10}H^9Br^3O$, thus obtained forms large lustrous crystals, insoluble in water, very slightly soluble in alcohol; it is decomposed by heat, decomposition commencing at about 100° C.; it is not further acted on by bromine.

When oil of anise is treated with *perchloride of tin* or *trichloride of antimony*, it thickens into a red pitchy mass, which, when boiled with water, deposits a white substance, apparently isomeric with anise-camphor. Cahours calls it *anisoin*. It is also formed when oil of anise is gradually mixed with $1\frac{1}{2}$ pts. strong sulphuric acid, and the resulting resinous mass treated with water. It is purified by solution in ether, and reprecipitation by dilute alcohol. Thus obtained, it is a white, inodorous solid which fuses a little above 100° C., and, when further heated, burns with a brilliant flame and an aromatic smell; it is heavier than water; insoluble in water, almost insoluble in alcohol, even on heating; more soluble in ether and volatile oils. It is soluble in strong sulphuric acid, forming a red solution, whence it is reprecipitated by water. It is not attacked by a boiling solution of caustic potash. When distilled, it partly volatilises unchanged and partly passes over as an isomeric oil. When crystallised from its ethereal solution, it forms very small white needles. The substance obtained by Will (Ann. Ch. Pharm. lxv. 230), by dropping oil of anise into a strong solution of *iodide of potassium saturated with iodine*, and treating the resulting magma with 6 or 8 times its volume of alcohol, is, according to Gerhardt, whose statement is confirmed by the recent experiments of Aelsmann and Kraut (*loc. cit.*), identical with anisoin. This substance, when treated with chlorine, yields a chlorine substitution-compound.—Anisoin is also produced by treating oil of anise with chloride of benzoyl. (Aelsmann and Kraut.)

When anise-camphor is distilled with *chloride of zinc*, a volatile oil passes over, which after a time generally deposits crystals, volatile without decomposition and not melting at 100° C. Both oil and crystals have the same composition as the original camphor; and the vapour-density of the oil is the same as that of the camphor. The oil is readily soluble in strong sulphuric acid, forming a fine crimson solution; the addition of water destroys the colour, but does not precipitate anything. By saturating the aqueous solution with carbonate of barium, a gummy salt is obtained, whose solution gives a dark violet colour with ferric salts; both acids and alkalis destroy the colour (Gerhardt). The same product is obtained when oil of anise or anise-camphor is treated with 3—4 pts. concentrated sulphuric acid, water added, the oil which separates filtered off, and the aqueous filtrate saturated with barytic carbonate. It appears to be identical with Laurent's *sulphodraconate of barium*, obtained by him from oil of tarragon.

2. *Oil of Tarragon* (Laurent, Revue Scient. x. 6) consists mainly of a camphor isomeric with that of anise, and behaving in the same manner with nitric and sulphuric acids and metallic chlorides. The proportion of liquid oil in this essence is very small: hence the crude oil does not boil below about 200° C., and the boiling point gradually rises to 206°, where it remains stationary. Its specific gravity is 0·945; vapour-density 6·157 at 230°. When treated with chlorine, it evolves heat and, acid vapours, and gradually becomes more syrupy; one of the products thus obtained (*chloride of draconyl*), of about the consistence of turpentine, gave on analysis percentages which seem to indicate the formula $C^{10}H^{16}Cl^2O.Cl^2$. When treated with alcoholic potash, this substance yielded a thick oil (*chlorodraconyl*) containing 42·5 per cent. carbon and 3·4 per cent. hydrogen.

3. *Oil of Bitter Fennel* (Cahours, *loc. cit*).—This essence is composed of two oils, the less volatile of which can readily be obtained pure by fractional distillation. Its composition is the same as that of anise-camphor; but it does not solidify at 10° C. Its specific gravity is somewhat less than that of water; it boils at 225° C. Treated with nitric acid, it behaves like anise-camphor; with bromine it gives a liquid viscous product, which is very difficult to purify. The more volatile oil appears to have the same composition as oil of turpentine. It boils about 190° C. When a stream of nitric oxide is led into it, it becomes thick and turbid, and on addition of alcohol of specific gravity 0·80, yields a white, silky precipitate, which is purified by repeated washing with alcohol. This substance, which forms fine crystalline needles, contains $3C^{10}H^{16},8NO$. It is discoloured when heated to 100° C., and at a higher temperature is entirely decomposed. It is scarcely soluble in alcohol of specific gravity 0·80, rather more in absolute alcohol, still more in ether; soluble in strong caustic potash, and reprecipitated by acids. When heated with caustic soda, it yields ammonia, an oil smelling like petroleum, and a gas which attacks the eyes. When treated with sulphydrate of ammonium in the cold, and then by an acid, it gives a precipitate which explodes slightly when heated; the filtrate gives an abundant blue precipitate with ferric salts. It dissolves in boiling sulphydrate of ammonium, forming a brown solution, and depositing sulphur, while a strong smell of oil of bitter-almonds is evolved. It is scarcely attacked by boiling hyposulphite of sodium. (Chiozza.) F. T. C.

ANISHYDRAMIDE. *Hydrure d'azoanisyl.* $C^{24}H^{24}N^2O^3$. (Cahours, Ann. Ch. Phys. [3] xiv. 487.)—The action of ammonia upon hydride of anisyl is analogous to that which it exerts upon the hydrates of benzoyl and salicyl, a hydramide being formed:

$$\underset{\text{Hydride of anisyl.}}{3C^8H^8O^2} + 2NH^3 = \underset{\text{Anishydramide.}}{C^{24}H^{24}N^2O^3} + 3H^2O$$

This substance is obtained by abandoning for some time a mixture of 1 vol. hydride of anisyl, and 4—5 vols. of a saturated aqueous solution of ammonia, in a closed vessel, when shining crystals of anishydramide gradually form, until, after some weeks, the whole becomes a semi-solid mass. The crystals are then freed from adhering liquid by pressure between folds of filtering paper, and dried. They are hard, snow-white prisms, very easily powdered; insoluble in water, soluble in boiling alcohol or ether, and in warm concentrated hydrochloric acid, whence they recrystallise on cooling. They melt at about 120° C. When anishydramide is acted on by sulphide of ammonium, a white powder is obtained, which Cahours (Compt. rend. xxv. 458) calls *thianisiol*, and Gerhardt (Traité, iii. 360) *hydride of sulphanisyl.* Its formula is C^8H^8SO.

For the probable constitution of anishydramide, see HYDRAMIDES in art. AMIDES, p. 177.

When anishydramide is kept for two hours at a temperature between 165° and 170° C., it is converted into an isomeric alkaloid, to which the name *anisine* has been given (Bertagnini, Ann. Ch. Pharm. lxxxviii. 128). In order to obtain this substance in a state of purity, it is dissolved in boiling alcohol, and hydrochloric acid added to the solution, when the hydrochlorate separates out in crystals. These are freed from the mother-liquor, decomposed by potash or ammonia, and the free base is recrystallised from alcohol. Thus obtained, anisine forms colourless transparent prisms, scarcely soluble either in hot or cold water, slightly soluble in ether, readily in alcohol. Its solution has a strong alkaline reaction and a bitter taste. Anisine forms crystallisable salts with acids. The *hydrochlorate*, $C^{24}H^{24}N^2O^3.HCl$, crystallises in colourless brilliant needles, slightly soluble in water, readily in alcohol. When dried at the ordinary temperature, they contain $4C^{24}H^{24}N^2O^3.HCl + 9H^2O$; they give off water at 100° C.

The *chloroplatinate*, $C^{24}H^{24}N^{2}O^{3},HCl,PtCl^{2}$, obtained by adding bichloride of platinum to the hydrochlorate, forms brilliant orange-coloured scales, slightly soluble in alcohol.

F. T. C.

ANISIC ACID. *Hydrate of anisyl. Draconic acid*, &c. $C^{8}H^{8}O^{3} = (C^{8}H^{6}O)''.H^{2}.O^{2}$. (Cahours, Ann. Ch. Phys. [3] ii. 287; xiv. 483; xxiii. 351; xxv. 21; xxvii. 439; Laurent, Revue Scient. x. 6, 362; Gerhardt, Ann. Ch. Phys. [3] vii. 292.)—This acid, discovered by Cahours in 1841, is a product of the oxidation of anise-camphor and of the crude oils of anise, fennel, and tarragon. The acids obtained from these several oils were at first distinguished by different names; but their identity is now clearly established. The first product of the oxidation of these substances is hydride of anisyl, which, by further oxidation, is converted into anisic acid. (See ANISYL, HYDRIDE OF.)

Cahours prepares anisic acid by boiling oil of anise with nitric acid of specific gravity 1·2 (23° Baumé), when a yellow resinous substance (*nitraniside*) is formed, together with anisic acid, which crystallises from the acid liquid on cooling. The crystals are washed with cold water, and dissolved in ammonia; the ammonium-salt is repeatedly crystallised till it is colourless, and then decomposed by acetate of lead; the difficultly soluble lead-salt is washed, and decomposed by sulphuretted hydrogen; and the anisic acid is dissolved from the sulphide of lead by boiling water, crystallised, and purified (if necessary) by sublimation.

Laurent's method of preparing it from oil of tarragon is as follows:—1 pt. oil together with a little water, is heated in a large retort, and 3 pts. common nitric acid are added gradually. The mixture thickens by degrees, and is finally converted into a brown, resinous, slightly crystalline mass. This is washed, and extracted with hot dilute ammonia, which dissolves all but a small quantity of a brown substance. The ammoniacal solution is evaporated to a syrup, when it deposits a further portion of the brown substance, which was held in solution by the free ammonia: if the evaporation be carried too far, the anisate and nitranisate of ammonium contained in the solution may be partially decomposed. The syrup is mixed with water, boiled, and filtered through animal charcoal; and the filtrate (neutralised, if acid, by ammonia) is evaporated, when anisate of ammonium crystallises in rhomboidal tables, while the nitranisate remains in the mother-liquor. The anisate is recrystallised two or three times from alcohol, dissolved in a boiling mixture of alcohol and water, and nitric acid added to the hot solution, which, on cooling, deposits crystals of anisic acid. These are further purified by recrystallisation from boiling alcohol, and, if necessary, by sublimation.

Anisic acid may also be prepared by dropping hydride of anisyl upon fused caustic potash. A soft resinous mass is obtained, which, when dissolved in water and saturated with hydrochloric acid, deposits crystals of anisic acid, which are purified as above. If hydride of anisyl be procurable, this is the most advantageous method, since the formation of nitranisic acid is entirely avoided. (Handwb.)

Anisic acid crystallises in brilliant colourless prisms, belonging to the monoclinic system, often of considerable size, with angles of 114° and 66°. The acute edges are mostly truncated; the base is replaced by two principal and three smaller faces. It has no taste or smell; is tolerably soluble in hot, but scarcely in cold, water; readily soluble in alcohol or ether, especially on boiling; its solution reddens litmus feebly. It fuses at 175° C, and solidifies on cooling to a crystalline mass; at a higher temperature it sublimes without decomposition into snow-white needles.

It is isomeric with salicylate of methyl.

It is violently attacked by chlorine and bromine (see below, SUBSTITUTION-PRODUCTS). Hot concentrated nitric acid converts it into nitranisic acid. Fuming nitric acid converts it into dinitranisol or trinitranisol (see ANISOL), the product varying with the duration of the reaction and the proportion of the reagents. If heat be applied, a third substance, chrysanisic acid, isomeric with trinitranisol, is simultaneously formed. A mixture of sulphuric and fuming nitric acids converts it into trinitranisol. Perchloride of phosphorus attacks it violently, forming chloride of anisyl, chloride phosphoryl, and hydrochloric acid. When distilled over caustic baryta, it is decomposed into carbonic anhydride and phenate of methyl (anisol).

$$C^{8}H^{8}O^{3} = CO^{2} + C^{6}H^{5}(CH^{3})O.$$

Anisates. Anisic acid is usually considered as monobasic; but it is probably diatomic, like glycollic and lactic acids. The general formula of the anisates is $C^{8}H^{7}MO^{3}$ (see ANISYL). They are mostly crystallisable: the alkaline and earthy salts are soluble, and the addition of a mineral acid separates anisic acid from their solutions.

The *aluminium-salt* crystallises slowly in fine needles, when a dilute solution of alum is added to anisate of ammonium.

The *ammonium-salt*, $C^{8}H^{7}(NH^{4})O^{3}$, is very soluble, and crystallises in large rhombic tables, the angles of whose base are 84° and 96°. Exposed to the air, they become opaque: heated to 99° C. in vacuo, they lose ammonia, pure anisic acid being left behind.

The *barium-salt*, when prepared directly by boiling anisic acid with baryta, crystallises first in needles, and then in rhomboidal scales. Chloride of barium does not precipitate anisate of ammonium immediately, but after some time, a difficultly soluble crystalline precipitate forms.

The *calcium-salt*. Chloride of calcium precipitates anisate of ammonium immediately; if the solutions are dilute, it crystallises in groups of needles.

The *copper-salt* is a bluish-white precipitate.

The *ferric-salt* is a yellow precipitate, composed of microscopic needles.

The *lead-salt* is a white precipitate, soluble in hot water, whence it crystallises on cooling in shining scales, which retain ½ atom of water after drying at 120°.

The *magnesium-salt* is soluble.

The *manganese-salt* crystallises slowly from a mixture of sulphate of manganese and anisate of ammonium.

The *mercuric*, *mercurous*, and *zinc-salts* are white precipitates; the first crystallises from hot water in microscopic needles.

The *potassium-salt* crystallises in rhomboidal or hexagonal tables; the *sodium-salt* in needles.

The *silver-salt* is a white precipitate, crystallising from hot water in fine needles, or pearly scales.

The *strontium-salt* crystallises gradually in small hexagonal or rectangular laminæ, from a mixture of chloride of strontium and anisate of ammonium.

ANISIC ETHERS. (Cahours, Ann. Ch. Phys. [3] xiv. 492.)

Anisate of Methyl, $C^9H^{10}O^3 = C^8H^7(CH^3)O^3$.—A mixture of 2 pts. anhydrous wood-spirit, 1 pt. anisic acid, and 1 pt. strong sulphuric acid, assumes an intense carmine-red colour; on the application of a gentle heat, wood-spirit first passes over, and then a heavy oil, which solidifies in the receiver. This is anisate of methyl. It is purified by washing with hot sodic carbonate, and with water, and recrystallisation from alcohol or ether. Thus prepared, it forms large, white, shining scales, which melt about 47° C., and solidify on cooling to a crystalline mass; at a higher temperature it distils undecomposed. It has a faint smell, resembling that of oil of anise, and a burning taste. It is insoluble in hot or cold water; readily soluble in alcohol or ether, especially on boiling. Unlike salicylate of methyl, it does not combine with potash or soda; but, when boiled with a strong solution of either alkali, is decomposed into methylic alcohol and an alkaline anisate. Aqueous ammonia does not dissolve it, but gradually decomposes it into methylic alcohol and anisamide, the latter of which crystallises out. Bromine, chlorine, and fuming nitric acid attack it violently, forming respectively the methyl-salts of the corresponding substitution-acid.

Anisate of Ethyl. $C^{10}H^{12}O^3 = C^8H^7(C^2H^5)O^3$.—When a solution of 1 pt. anisic acid in about 6 pts. absolute alcohol is saturated at about 60° C. with hydrochloric acid gas, a fuming liquid is obtained, whence water precipitates only anisic acid. On distilling this liquid chloride, hydrate, and finally anisate of ethyl pass over; and on adding water to the distillate, the latter product separates out as a heavy oil, which is washed with sodic carbonate, dried over chloride of calcium, and rectified over oxide of lead. It is a colourless oily liquid, heavier than water, with a smell like that of oil of anise, and a warm aromatic taste. It boils between 250° C. and 255°, is insoluble in water, readily soluble in alcohol and ether. It may be kept unchanged in closed vessels; but, when exposed to the air, it gradually becomes acid. Its decompositions are precisely analogous to those of the methyl-salt.

Substitution-derivatives of Anisic Acid.

BROMANISIC ACID. *Bromodraconesic acid* (Laurent). $C^8H^7BrO^3$.—When powdered anisic acid is treated with bromine, heat is evolved, together with abundance of hydrobromic acid; the product is washed with water, and crystallised from boiling alcohol. Bromanisic acid is thus obtained in white shining needles, slightly soluble in hot water, readily in hot alcohol or ether. It melts at 205° C., and sublimes in iridescent laminæ. When distilled with lime, it yields carbonic anhydride and bromanisol. The alkaline bromanisates are soluble; the potassium and sodium-salts yield bromanisol by dry distillation. In their solution, lead-, silver-, barium-, strontium-, and calcium-salts give white precipitates; the last three are not quite insoluble, but crystallise gradually from dilute solutions.

Bromanisate of Methyl, $C^8H^6(CH^3)BrO^3$, is obtained by dropping bromine on the anisate, and treating the yellowish-red product as in the case of bromanisic acid. Also in the same manner as the anisate, bromanisic being substituted for anisic acid. The mixture is boiled in a water-bath for a quarter of an hour, and water added, when the bromanisate separates in flakes, which are washed with dilute ammonia and crystallised from hot alcohol. It forms colourless transparent prisms, which melt at a gentle heat: it is insoluble in water; soluble, especially on heating, in alcohol and wood-spirit; less soluble in ether. By boiling potash it is decomposed like the anisate.

Bromanisate of Ethyl, $C^8H^6(C^2H^5)BrO^3$, is obtained by the same process as anisate of ethyl, anisic being replaced by bromanisic acid; or by treating anisate of ethyl with bromine. It is purified in the same way as the methyl-salt. It forms long, white, shining needles, insoluble in water, soluble in alcohol or ether: it fuses at a gentle heat, and sublimes undecomposed. It is decomposed by boiling potash, and is not attacked by excess of bromine.

CHLORANISIC ACID, $C^8H^7ClO^3$, is obtained by passing chlorine over anisic acid in fusion; the product is washed with water, and crystallised from alcohol of 95 per cent. It forms fine shining needles, scarcely soluble in water, readily in alcohol or ether. It melts at about 176° C., and may be sublimed without decomposition. It is not acted upon by chlorine, even in sunshine. Strong sulphuric acid dissolves it by aid of gentle heat; it recrystallises from the solution on cooling, or is at once precipitated by water. When heated with baryta, it is decomposed like anisic acid. The metallic chloranisates resemble the corresponding bromanisates in solubility and general properties. The *chloranisates of methyl* and *ethyl* are obtained by submitting the corresponding anisates to the action of dry chlorine; the latter may also be prepared in a similar way to anisate of ethyl. Both are crystalline compounds, insoluble in water, soluble in alcohol or ether, and decomposed by boiling potash.

NITRANISIC ACID, $C^8H^7(NO^2)O^3$, is formed by the action of strong warm nitric acid on anisic acid. It is usually prepared by boiling oil of anise with nitric acid of specific gravity 1·33 (36° Baumé), until the oily substance which first forms has completely disappeared. The addition of water then precipitates yellowish flakes of impure nitranisic acid. This is purified by washing with water, dissolving in ammonia, recrystallising the ammonium-salt till it is colourless, dissolving it in water, precipitating the acid by nitric or hydrochloric acid, and washing it repeatedly with water. It is also formed in Laurent's process for preparing anisic acid from oil of tarragon, remaining in the ammoniacal mother-liquor whence anisate of ammonium has crystallised out. It is obtained thence by adding nitric acid, washing the precipitate, and boiling it for half an hour with nitric acid; the acid solution deposits on cooling short prisms of nitranisic acid, which are washed with water, and crystallised from hot alcohol. Nitranisic acid crystallises in small shining needles, of a slight yellow tinge, without taste or smell. It is scarcely soluble even in hot water; readily in alcohol or ether. It melts between 175° and 180°. When carefully heated further, it partly sublimes, partly blackens, and is decomposed; if heated suddenly, it decomposes at once, with evolution of light. It is not attacked by chlorine, bromine, or strong nitric acid; by fuming nitric acid, it is acted on in the same way as anisic acid. When heated with perchloride of phosphorus, it yields a dark yellow oil, with a very high boiling point, which is probably chloride of nitranisyl, $C^8H^6(NO^2)O^2,Cl$ (Cahours). An alcoholic solution of sulphide of ammonium converts it into anisamic acid (p. 291). According to Laurent (*loc. cit.*) nitranisic acid combines, atom for atom, with anisic, chloranisic, and bromanisic acids, forming peculiar dibasic acids.

The alkaline *nitranisates* are soluble and crystallisable: the ammonium-salt crystallises in fine needles, grouped in spheres; it is soluble in alcohol. The alkaline-earthy nitranisates are difficultly soluble; those of the heavy metals generally insoluble.

Nitranisate of methyl is prepared by a process analogous to that described in the case of anisate of methyl; or by dissolving anisate of methyl in fuming nitric acid, adding water, and crystallising the precipitate from alcohol. It forms beautiful large shining tables of a yellowish hue. It is insoluble in water; readily soluble in hot alcohol or wood-spirit, whence it separates almost completely on cooling. It melts at about 100° C., and sublimes undecomposed.

Nitranisate of ethyl is prepared either by dissolving anisate of ethyl in an equal volume of fuming nitric acid, or by a process analogous to that described in the case of anisate of methyl. In the latter case, the mixture must be kept at a temperature of 60°—70° C., while it is saturated with hydrochloric acid. The compound is precipitated by water, washed with dilute ammonia, and crystallised from alcohol. It exactly resembles the methyl-salt in appearance, and solubility in water and alcohol, and melts between 98° and 100° C. Strong sulphuric acid dissolves it in the cold, more readily on heating; it partly recrystallises as the solution cools, and is completely precipitated by water. Bromine exerts no action upon it.

Trinitranisic Acid, $C^8H^5(NO^2)^3O^3$, is obtained by treating anisic acid in the cold with a mixture of fuming nitric and fuming sulphuric acid, and diluting the mixture with 8 to 10 times its volume of water. It forms very beautiful salts with the alkalis, especially with ammonia and potash.

SULPHANISIC ACID, $C^8H^8O^3,SO^3$. (Zervas, Ann. Ch. Pharm. ciii. 339; Limpricht, Gm. Handb. xiii. 128.)—Obtained by heating anisic acid with common sulphuric acid to 110° C. or with fuming sulphuric acid to 100°, diluting the mixture with water, adding carbonate of lead, filtering at the boiling heat, and boiling the insoluble residue with water as long as the filtered liquid yields crystals of the lead-salt on cooling. These, when decomposed by sulphuretted hydrogen, yield the acid (Zervas). Limpricht treats anisic acid with sulphuric anhydride.

Sulphanisic acid, obtained by slow evaporation of the aqueous solution, forms needles which are permanent in the air, and give off 6·9 per cent. (1 at.) water at 100° C., and suffer no further decomposition below 170°. The aqueous solution may be boiled without decomposition.

Sulphanisic acid is dibasic. The *sulphanisates* of ammonium, potassium, and sodium crystallise readily, the first in long slender needles. The *barium-salt*, $C^8H^6Ba^2O^3.SO^3 + 8H^2O$, obtained by saturating the acid with carbonate of barium, forms fine crystals, which, after drying over sulphuric acid, give off 16·9 per cent. (8 at.) water at 180° C. It dissolves easily in water, and is precipitated by alcohol. The *magnesium-salt* forms very soluble needles. The *normal lead-salt*, $C^8H^6Pb^2O^3.SO^3 + 8H^2O$, forms beautiful needles, which give off their water at 180° C. The *acid lead-salt*, $C^8H^7PbO^3.SO^3 + H^2O$, forms nodular crystals; easily soluble in water.

The *silver-salt* forms nodular crystals, sparingly soluble in water. According to Zervas, the solubility of the barium and lead-salts is diminished by repeated crystallisation. F. T. C.

ANISIC ALCOHOL. *Hydrate of Anisalyl*, $C^8H^{10}O^2 = C^8H^9O.H.O$. (Cannizzaro and Bertagnini, Ann. Ch. Pharm. xcviii. 188.)—Formed from hydride of anisyl in the same way as benzoic alcohol from hydride of benzoyl. When a solution of pure hydride of anisyl in an equal volume of alcohol is mixed with three times its bulk of alcoholic potash of about 7° Beaumé (specific gravity 1·052), a slight evolution of heat takes place, and anisic alcohol and anisate of potassium are formed, the latter in such quantity that the mixture shortly becomes a crystalline pulp. ($2C^8H^8O^2 + KHO = C^8H^7KO^3 + C^8H^{10}O^2$.) After 10 or 12 hours, the alcohol is distilled off in a water-bath, and the residue is suspended in water, and extracted with hot ether. On evaporating the ethereal solution, a brown oil is obtained, and on distilling the oil, anisic alcohol passes over at about 260°C., as a colourless liquid, which crystallises on cooling. This product generally contains some hydride of anisyl, which may be detected by agitating it with a concentrated solution of acid sulphite of sodium (see ANISYL, HYDRIDE OF). To purify it, it is treated again with a small quantity of alcoholic potash, distilled in carbonic anhydride, and the crystalline distillate pressed between filter-paper.

Anisic alcohol crystallises in hard, white, shining needles. It distils undecomposed between 248° and 250° C., and melts at 23°, when anhydrous, but at much lower temperatures when moist. It is heavier than water, has a faint spirituous, sweetish smell, and a burning taste like that of oil of anise. At ordinary temperatures, it remains unaltered in the air; but when heated nearly to its boiling point it, absorbs oxygen, and is converted into hydride of anisyl. Oxidising agents (as platinum-black, nitric acid, &c.) convert it, first into hydride of anisyl, then into anisic acid. Potassium dissolves in it with evolution of hydrogen. Sulphuric acid, even when moderately concentrated, or phosphoric anhydride, converts it into a resinous mass Heated with chloride of zinc, it yields water, and an oily liquid, which solidifies on cooling into a hard, transparent, vitreous mass, which melts at 100° C., and is insoluble in water and alcohol, but soluble in bisulphide of carbon.

When treated with hydrochloric acid gas, it forms water and a colourless liquid, having a fruity smell and a burning taste. This substance is its hydrochloric ether, or *chloride of anisalyl*, $C^8H^9O.Cl$, and is decomposed by alcoholic ammonia yielding chloride of ammonium, and the hydrochlorates of anisamine and dianisamine (p. 297).

If, as is probable from its analogy to salicylic acid, anisic acid be regarded as dibasic, anisic alcohol becomes diatomic, $(C^8H^8).H^2.O^2$; and chloride of anisalyl will be

$C^8H^8\left\{\begin{matrix}HO\\Cl\end{matrix}\right.$, analogous to glycolic chlorhydrin. F. T. C.

ANISIC ANHYDRIDE. $C^{16}H^{14}O^5 = C^8H^7O^2.C^8H^7O^2.O$. (Pisani, Ann. Ch. Pharm. cii. 284.)—Formed by the action of oxychloride of phosphorus on dry anisate of sodium; the mass is washed with water, and the insoluble residue crystallised from ether. It forms silky needles, soluble in alcohol or ether, insoluble in water or aqueous alkalis; it melts at 99°C., and distils at a higher temperature. By long boiling with water or aqueous alkalis, it is converted into anisic acid. F. T. C.

ANISIDINE (*Methylphenidine*, Gerh.) $C^7H^9NO = N.C^7H^7O.H^2$. (Cahours. Ann. Ch. Phys. [3] xxvii. 443.)—The action of sulphide of ammonium on the nitro-derivative of anisol gives rise to the formation of peculiar organic bases. Anisidine is obtained by dissolving nitranisol in an alcoholic solution of sulphide of ammonium, evaporating at a gentle heat to a quarter of its volume, adding a slight excess of hydrochloric acid to the brown residue, separating the sulphur by addition of water, and filtering. The yellow-brown filtrate deposits on evaporation, needles of hydrochlorate of anisidine, which are dried with filter paper and distilled with a strong solution of potash, when anisidine passes over with the aqueous vapour in the form of an oil, which solidifies on cooling.

The properties of anisidine but are imperfectly known. It combines with acids, forming salts. The *hydrochlorate* forms fine colourless needles, soluble in water and alcohol. When a hot concentrated solution of this salt is mixed with a concentrated solution of dichloride of platinum, the *chloroplatinate* separates on cooling in yellow needles. The *nitrate*, *sulphate*, and *oxalate* are crystallisable.

The products of the action of sulphide of ammonium on the higher nitro-derivatives of anisol may be regarded as nitro-derivatives of anisidine, though it is not known whether they can be formed by the action of nitric acid on anisidine.

NITRANISIDINE (*Methylnitrophenidine*, Gerh.) $C^7H^8N^2O^3 = C^7H^8(NO^2)NO$.—Prepared by a process similar to that described for anisidine, dinitranisol being substituted for nitranisol. The filtrate is mixed with ammonia, and the precipitate thus formed is washed with water, and crystallised from boiling alcohol. Nitranisidine forms long, garnet-red, shining needles, which are insoluble in cold, soluble in boiling, water; soluble in boiling alcohol, whence it separates almost entirely on cooling; also in ether, especially if heated. It melts at a gentle heat, and on cooling forms a radiated mass; when heated gradually to a higher temperature, it gives off yellow fumes, which condense into yellow needles. Bromine attacks it violently, forming a resinous mass, which has no alkaline properties. Fuming nitric acid decomposes it violently, yielding a viscous mass, insoluble in acids. The chlorides of benzoyl, cinnamyl, cumyl, and anisyl attack it when gently heated, forming hydrochloric acid, and compounds analogous to benzamide, which are described by Cahours under the names of *benzonitraniside*, $C^{14}H^{12}N^2O^4 = N.C^7H^5O.C^7H^6(NO^2)O.H.$, *cinnitraniside*, $C^{16}H^{14}N^2O^4$, &c. These bodies are obtained pure by successively washing the products of these reactions with water, hydrochloric acid, and dilute potash, and crystallising from boiling alcohol; they are insoluble in water or in cold alcohol.

Nitranisidine dissolves readily in acids, and with many of them forms crystalline salts. The *hydrochlorate* and *hydrobromate*, when pure, form colourless needles, slightly soluble in cold, readily in boiling, water. The *chloroplatinate* separates in orange-brown needles from a mixture of hot concentrated solution solutions of the hydrochlorate and dichloride of platinum. The *sulphate* forms concentric groups of silky needles, readily soluble in water, especially in water containing sulphuric acid. The *nitrate* forms large needles, much more soluble in hot than in cold water.

Dinitranisidine (*Methyl-dinitrophenidine*, Gerh.) $C^7H^7N^3O^5 = C^7H^4(NO^2)^2NO$.—Prepared precisely like nitranisidine, trinitranisol being substituted for dinitranisol. When dry, it is an amorphous powder, of a bright red or violet-red colour, according to the concentration of the solution from which it was precipitated. It is almost insoluble in cold water, very slightly in hot water, forming an orange solution: slightly soluble in cold, moderately in hot alcohol, and separates on cooling in violet-black crystals; slightly soluble in hot ether. It melts at a gentle heat, and solidifies on cooling into a radiated, violet-black, crystalline mass. It is much less basic in its properties than the foregoing compound: it forms crystallisable salts with hydrochloric, nitric, and sulphuric acids, if the acids be employed in excess, but these compounds are decomposed by water. When heated with fuming nitric acid, it is violently attacked, and yields a yellowish brown resinous mass, which dissolves in potash, forming an intensely brown solution. F. T. C.

ANISINE. See ANISHYDRAMIDE.

ANISOIC ACID. $C^{10}H^{10}O^6$. (Limpricht and Ritter, Ann. Ch. Pharm. xcvii. 364.)—A product of the oxidation of oil of star-anise (probably also of oil of anise, tarragon, fennel, &c.). The oil is heated with nitric acid, of specific gravity 1·2, and the oily layer which sinks to the bottom of the mixture is agitated with a warm solution of acid sulphite of sodium, whence anisoate of sodium crystallises on cooling. To the purified crystals, enough sulphuric acid is added to decompose the salt, the whole evaporated to dryness, and the acid extracted from the residue by absolute alcohol. It crystallises from its aqueous solution in small laminæ, which have a strong acid reaction, and are very soluble in water, alcohol, and ether; they melt at about 120° C., and are not volatile without decomposition.

Anisoates are mostly readily soluble. The *sodium-salt*, $C^{10}H^{11}NaO^6$, and the *barium-salt*, form white crystalline nodules. The *silver*-salt forms soluble nodules, and speedily blackens when moist. F. T. C.

Städeler and Wächter (Ann. Ch. Pharm. cxvi. 169) regard this acid as identical with *thianisoic acid*, $C^{10}H^{14}SO^4$, the product which they obtain by treating anise-camphor with nitric acid of specific gravity 1·106, then distilling and agitating the distillate with acid sulphite of sodium and alcohol. The atomic weights of the two acids are nearly equal (anisoic acid = 234; thianisoic acid = 230), so that the determinations of carbon and metal in Limpricht and Ritter's analyses of the silver and barium-salts will agree with the one formula as well as with the other. Moreover in Limpricht and Ritter's analyses of both these salts, the amount of hydrogen found was much too low for the formula of anisoic acid (in the barium-salt 5·44 per cent., by calculation 5·65; in the silver-salt 4·0 per cent., calculation 4·98), and the absence of sulphur was not established by direct experiment. (See THIANISOIC ACID.)

ANISOIN. See ANISE, OIL OF.

ANISOL. *Phenate of methyl. Dracol.* $C^7H^8O = C^6H^5(CH^3)O$. (Cahours, Ann. Ch. Phys. [3] ii. 274; x. 353; xxvii. 439.)—This compound is formed by the action of caustic baryta on anisic acid, or on its isomer, salicylate of methyl: also directly from phenic acid, by the substitution of methyl for 1 at. hydrogen. It may be obtained in various ways. Anisic acid distilled with excess of caustic baryta or lime, is decomposed, anisol passing over as a volatile oil: $C^8H^8O^3 + Ba^2O = C^7H^8O + CO^3Ba^2$. The same result follows when salicylate of methyl is dropped on finely powdered baryta, and the mixture gently distilled. A third method is to heat phenate of potassium with iodide of methyl in a sealed tube, to 100°—120° C. $C^6H^5KO + CH^3I = C^6H^5(CH^3)O. + KI$. The product of either of these reactions is washed with dilute potash and with water, and rectified over chloride of calcium.

Anisol is a colourless, very mobile liquid, with a pleasant aromatic smell. It is insoluble in water, very soluble in alcohol and ether, insoluble in potash. Its specific gravity at 15° C. is 0·991; it boils at 152° C., and distils undecomposed. It is isomeric with benzoic alcohol and taurylic acid.

It may be distilled over phosphoric anhydride without decomposition. It dissolves entirely in strong sulphuric acid, and is not precipitated by water, a copulated acid being formed. This acid, which Cahours calls *sulphanisolic*, and Gerhardt *methyl-sulphophenic* acid, has the formula $C^7H^8SO^4$. By saturating the acid liquid with carbonate of barium, a crystalline barium-salt is obtained, which contains 1 at. barium. If fuming sulphuric acid be employed, not in excess, the addition of water separates crystalline flakes of a neutral body, which Cahours calls *sulphanisolide*. Its formula is $C^{14}H^{14}SO^4$; it is to sulphanisolic acid as sulphate of ethyl is to ethyl-sulphuric acid. This body is best obtained by passing the vapour of sulphuric anhydride into artificially cooled anisol, and adding water to the mixture; sulphanisolide is then deposited in fine needles, which are recrystallised from alcohol, while sulphanisolic acid remains in solution. It forms soft silvery prisms, insoluble in water, soluble in alcohol and ether. It melts at a gentle heat, and sublimes undecomposed. Strong sulphuric acid converts it into sulphanisolic acid.

SUBSTITUTION-DERIVATIVES OF ANISOL.—Chlorine and bromine form with anisol crystalline substitution-compounds. The chlorine-compounds have not been examined; there are two bromine-compounds, *bromanisol*, C^7H^7BrO, and *dibromanisol*, $C^7H^6Br^2O$. The latter is soluble in boiling alcohol, whence it crystallises in brillant scales. It melts at 54° C., and at a higher temperature sublimes entirely in small shining tables.

Fuming nitric acid acts energetically on anisol, forming three distinct nitro-compounds, *Nitranisol*, *Dinitranisol*, and *Trinitranisol*, according to the proportions of the reagents and the duration of the reaction. *Nitranisol*, $C^7H^7(NO^2)O$, is prepared by adding fuming nitric acid by small portions to anisol, the mixture being kept cool by ice. A bluish-black oily liquid is thus obtained, which is washed with dilute potash, and rectified over chloride of calcium. Anisol distils over first, and when the boiling point remains constant at about 260° C., the receiver is changed. Nitranisol is a clear amber-coloured liquid, heavier than and insoluble in water, with an aromatic smell, something like that of bitter-almond oil. It boils between 262° and 264° C. It is not attacked by aqueous potash, even on heating. When gently heated with strong sulphuric acid, it dissolves, and separates out again on the addition of water. When heated with fuming nitric acid, it is successively converted into di- and tri-nitranisol.

Dinitranisol, $C^7H^6(NO^2)^2O$, is prepared by boiling anisol for a few minutes with excess of fuming nitric acid: on adding water, a yellow liquid is separated, which soon solidifies into a yellow mass, which is recrystallised from boiling alcohol. It is also obtained by heating anisic acid to 90°—100° C., for about half an hour, with two or three times its weight of fuming nitric acid: chrysanisic acid forms at the same time, and is removed by dilute potash. Dinitranisol crystallises in long pale yellow needles, insoluble even in boiling water, soluble in alcohol and ether. It melts at about 86° C., and sublimes undecomposed. Aqueous potash does not attack it, even on boiling, unless the solution be very strong, and even then long boiling is required: when boiled with alcoholic potash, it is speedily decomposed, dinitrophenate of potassium being formed.

Trinitranisol, $C^7H^5(NO^2)^3O$, is formed when anisol, anisic, or nitranisic acid is heated with a mixture of equal parts of strong sulphuric and fuming nitric acid. Anisic acid is generally employed for its preparation. The mixture, which at first is clear and colourless, is gently heated till it begins to become turbid, carbonic anhydride being copiously given off. The heat is then removed, when there gradually collects on the surface an oil, which solidifies on cooling. A large quantity of water is then added, and the solid product is washed with boiling water, and crystallised from a mixture of equal parts of alcohol and ether. The reaction is complete if 15 pts. of the mixed acids be employed for 1 pt. anisic acid. Trinitranisol crystallises in yellowish, very brilliant tables, insoluble in water, soluble in hot alcohol or in ether. It melts at 58°—60° C., and if carefully heated, sublimes. Warm sulphuric or nitric acid dissolves without decomposing it. Aqueous ammonia or dilute potash, does not attack it, even on boiling; but moderately strong aqueous potash gives it an intense brown-red colour, and completely decomposes it on boiling, forming a slightly soluble potassium-salt of an acid, which is isomeric with, but, according to Cahours, distinct from picric, or trinitrophenic acid, which he designates picranisic acid.

All the nitro-derivatives of anisol are readily attacked by alcoholic sulphide of ammonium, sulphur being separated, and anisidine and its nitro-derivatives being formed.
F. T. C.

ANISULMIN. The name given by Brandes and Reimann to a brown product, obtained by extracting anise-seed, after previous treatment with alcohol, water, and hydrochloric acid, with aqueous potash, and precipitating the alkaline solution by acetic acid.
F. T. C.

ANISURIC ACID. $C^{10}H^{11}NO^4$.—An acid analogous to hippuric acid, produced by the action of chloride of anisyl on the silver-compound of glycocoll ($C^2H^4AgNO^2 + C^8H^7O^2Cl = AgCl + C^{10}H^{11}NO^4$). Acids, with aid of heat, convert it into glycocoll and anisic acid. (Cahours, Ann. Ch. Pharm. ciii. 90.)

ANISYL. $C^8H^7O^2$.—A hypothetical radicle, supposed to be contained in anisic acid, hydride of anisyl, and other anisic compounds. It may be regarded as salicyl, $C^7H^5O^2$, in which 1 at. hydrogen is replaced by methyl, $C^8H^7O^2 = C^7H^4(CH^3)O^2$: and, in fact, anisic acid and salicylate of methyl are not only isomeric compounds, but are both decomposed in the same manner by caustic baryta. Anisic acid is, therefore, to salicylic acid, as acetic is to formic acid. If, as Piria's recent researches (Ann. Ch. Pharm. xciii. 262) tend to show, salicylic acid be not monobasic but dibasic, the clear analogy between it and anisic acid, would probably lead to the conclusion that the latter acid is also dibasic; in which case, all anisic compounds must be regarded as containing a diatomic radicle, C^8H^6O, rather than a monatomic radicle, $C^8H^7O^2$.

BROMIDE OF ANISYL. $C^8H^7O^2.Br$. (Cahours, Ann. Ch. Phys. [3] xiv. 486.)—Prepared by dropping dry bromine (excess of which must be avoided), upon hydride of anisyl: heat is evolved, hydrobromic acid given off, and the mixture solidifies. The solid product is rapidly washed with ether, pressed between filter-paper, and crystallised from ether. It forms white, silky crystals, which are volatile without decomposition. Strong boiling potash gradually converts it into anisate and bromide of potassium.

CHLORIDE OF ANISYL. $C^8H^7O^2.Cl$. (Cahours, Ann. Ch. Phys. [3] xxiii. 351.)—When dry anisic acid is treated in a retort with pentachloride of phosphorus, a violent action takes place, and a mixture of products passes into the receiver. These are fractionally distilled, that part which boils between 250° and 270° C. being collected apart, washed with a little water, and rectified over chloride of calcium. Chloride of anisyl also seems to be formed by the action of chlorine on the hydride. It is a colourless liquid, with a strong smell: its boiling point is 262° C.; its specific gravity it 1·261 at 15°. When exposed to moist air, it is speedily decomposed into hydrochloric and anisic acids. In contact with dry ammonia, it evolves heat, and is converted into anisamide (*q. v.*). Alcohol and wood-spirit attack it energetically, forming hydrochloric acid, and anisate of ethyl and methyl respectively.

HYDRIDE OF ANISYL, $C^8H^8O^2 = C^8H^7O^2.H$. *Anisylwasserstoff; Anisylous Acid; Anisic Aldehyde; Anisal.* (Cahours, Ann. Ch. Phys. [3] xiv. 484; xxiii. 354.) —Formed, together with anisic acid, by the oxidation of oil of anise, or of anisic alcohol; in the latter case, the action of platinum-black is sufficient to produce the effect. It is prepared by gently heating oil of anise for about an hour, with three times its volume of nitric acid of specific gravity 1·106 (14° Baumé): the heavy oil which is thus formed is washed with dilute potash, and distilled. The distillate is agitated with a warm solution of acid sulphite of sodium, of specific gravity 1·25; the crystalline compound thus formed is collected on a funnel, thoroughly washed with alcohol, dissolved in as little hot water as possible, and the solution heated with excess of strong sodic carbonate, when the hydride of anisyl separates out and floats on the surface. It is then purified by redistillation. The reaction is as follows, oxalic acid being simultaneously formed:

$$\underset{\text{Oil of anise.}}{C^{10}H^{12}O} + O^6 = \underset{\substack{\text{Hydride}\\\text{of anisyl.}}}{C^8H^8O^2} + \underset{\substack{\text{Oxalic}\\\text{acid.}}}{C^2H^2O^4} + H^2O$$

Hydride of anisyl is a yellowish liquid, with a burning taste, and an aromatic smell somewhat like that of hay: its specific gravity at 20° C. is 1·09, and its boiling-point 253°—255° C. It is almost insoluble in water, but soluble in all proportions in alcohol and ether. Strong sulphuric acid dissolves it, forming a dark-red solution, whence it is reprecipitated by water. When exposed to the air, it gradually absorbs oxygen, and is converted into anisic acid; the same change is produced more rapidly by means of oxidising agents, such as platinum-black, or dilute nitric acid. Strong nitric acid converts it into nitranisic acid. Strong aqueous potash does not dissolve it till after long boiling; fused or alcoholic potash convert it into anisate, with evolution of hydrogen, or formation of anisic alcohol. Prolonged contact with caustic ammonia converts it into anishydramide (*q. v.*). Pentachloride of phosphorus attacks it energetically, the mixture thickening, and finally becoming a black pitchy mass, and a scanty distillate is obtained, consisting of chloride of phosphoryl, together with a neutral oil having a strong smell of turpentine.

Hydride of anisyl possesses the property peculiar to aldehydes, of forming crystalline compounds with acid sulphites of alkali-metal. *Sulphite of anisyl-sodium*, $C^8H^7NaO^2,SO^3 + aq.$ (Bertagnini, Ann. Ch. Pharm. lxxxv. 268), is obtained by agitating hydride of anisyl with a strong solution of acid sulphite of sodium: the mixture assumes the consistence of butter, and finally becomes crystalline. When dried and recrystallised from boiling alcohol, it forms colourless, shining scales; but it is always partially decomposed during crystallisation. It is soluble in cold water, and is reprecipitated by acid sulphite of sodium, in which it is almost insoluble: its aqueous solution is decomposed by boiling, hydride of anisyl being formed and sulphurous anhydride evolved. Acids and alkalis decompose it also. Ammonia dissolves it, forming oily drops which gradually solidify into crystals of anishydramide. Iodine and bromine decompose it readily. The potassium- and ammonium-compounds are similar to the sodium-compound, both in mode of formation and in general properties. F. T. C.

ANKERITE. A variety of dolomite, CO^3CaMg, in which the magnesium is partly replaced by iron and manganese. According to Berthier (Pogg. Ann. xiv. 103), it fuses to a crystalline compound with carbonate of sodium.

ANNABERGITE. See NICKEL-GREEN.

ANNEALING. (*Tempering, Récuit, Anlassen.*)—Many bodies when raised to a high temperature and quickly cooled, become very hard and brittle. This is a great inconvenience in glass, and also in steel, when this metallic substance is required to be soft and flexible. These inconveniences are avoided by cooling the substance very gradually; and the process is called annealing. Glass vessels, or other articles, are carried into an oven or apartment near the great furnace, called the *leer*, where they are permitted to cool, more or less quickly, according to their thickness and bulk. The annealing or tempering of steel, or other metallic bodies, consists simply in heating them, and suffering them to cool again, either upon the hearth of the furnace, or in any other situation where the heat is moderate, or at least the temperature is not very low.—U. (See *Dictionary of Arts, Manufactures, and Mines*, i. 162.)

ANNOTTO. The pellicles of the seeds of the *Bixa orellana*, a liliaceous shrub, from 15 to 20 feet high in good ground, afford the red masses brought into Europe under the name of *annotto*, *anatto*, *arnatto*, *arnotto*, *orlean*, and *roucou*.

The annotto commonly met with in this country is moderately hard, of a brown colour on the outside and a dull red within. It is difficultly acted upon by water, and tinges the liquor of a pale brownish-yellow colour. In rectified spirit of wine, it dissolves very readily, and communicates a high orange or yellowish-red colour

Hence it is used as an ingredient in varnishes, for giving more or less of an orange cast to the simple yellows.

Ether is the best solvent of annotto. Potash and soda, either caustic or carbonated, disolve annotto in large quantity, from which solutions it is thrown down by acids in small flocks. The alkaline solutions are of a deep red colour. Chlorine decolorises the alcoholic solution of annotto, the liquid becoming speedily white and milky. If strong sulphuric acid be poured on annotto in powder, the red colour passes immediately to a very fine indigo blue: but this tint is not permanent, changing to green, and finally to violet, in the course of twenty-four hours. This property of becoming blue belongs also to saffron. Nitric acid, slightly heated on annotto, sets it on fire, and a finely divided charcoal remains. Annotto is soluble both in essential oils, as oil of turpentine, and in fixed oils. (Boussingault, Ann. Ch. Phys. xxviii. 440.)

Annotto contains a crystalline yellow colouring matter, called *bixin* (*q.v.*), which, when treated with alkalis, in contact with air, absorbs oxygen, and is converted into a red substance called *bixein*. Annotto is used in dyeing, but the colours produced by it are all fugitive; also for colouring cheese.—U. (See *Ure's Dictionary of Arts, Manufactures, and Mines*, i. 178.)

ANODE. Faraday's term for the positive pole or electrode in the voltaic circuit. (See ANION and ELECTRICITY.)

ANORTHITE. $Ca^2O.SiO^2 + Al^4O^6.SiO^2 = (Ca\,al^{ii})SiO^4$.—A mineral belonging to the felspar family. It occurs in small crystals belonging to the triclinic system; also massive, with granular, columnar, or coarsely lamellar structure. Cleaves perfectly in two directions, inclined to one another at 85° 48′. Specific gravity 2·66—2·78. Hardness = 6—7. Transparent to translucent, with white, greyish or reddish colour, and vitreous lustre. Streak uncoloured. Fracture conchoïdal. Brittle. Before the blowpipe it melts, and forms with soda a milk-white enamel. Strong hydrochloric acid decomposes it completely, but does not gelatinise it.

Anorthite is found on Vesuvius and Somma, in the island of Procida, in Corsica, near Bogoslowsk in the Ural, on Hecla and in other localities in Iceland, in Java, in the island of St. Eustache in the Antilles, and in the meteorite of Juvenas. The follow- are analyses:

	G. Rose. Somma.	Deville. Antilles.	Damour. Hecla.	Waltershausen. Hecla.	Potyka. Ural.
SiO^2	44·49	45·8	45·97	45·14	46·79
Al^4O^6	34·46	35·0	33·28	32·11	33·16
Fe^4O^6	0·74	—	1·12	2·03	3·04
Ca^2O	15·68	17·7	17·21	18·32	15·97
Mg^2O	5·26	0·9	—	—	—
Na^2O	—	0·8	1·85	1·06	1·28
K^2O	—	—	—	0·22	0·55
Ni^2O and Co^2O	—	—	—	0·77	—
Water	—	—	—	0·31	—
	100·63	100·2	99·43	99·96	100·79

The formula above given, which is that of an orthosilicate, requires 43·2 SiO^2, 36·8 Al^2O^6, 20·0 Ca^2O.

The following are varieties of anorthite having nearly the same composition and crystalline form:—1. *Amphodelite* has the structure and specific gravity of anorthite; found at Logi, in Finland, and Tunaberg in Sweden.—2. *Bytownite*, from Bytown in Canada.—3. *Diploite* or *Latrobite*, from the island Amitok on the coast of Labrador. Rose-red, with the form, structure, and density of anorthite.—4. *Indianite*, from Hindostan. Granular masses, having the structure of felspar.—5. *Lepolite*, from Logi and Orijarfvi in Finland. Resembles amphodelite.—6. *Lindsayite*, from the same localities, appears to be the same altered, and containing a few per cent. of water.—7. *Polyargite*, from Tunaberg. Rose-red; granular; gives off water when heated, and becomes colourless.—8. *Rosellan*, from Åker, Södermanland. Exhibits similar properties.—9. *Sundvilkite*, from Kimito, Finland. Has the form of felspar; and specific gravity = 2·70.—10. *Wilsomite*, from Canada. Rose-red; specific gravity 2·76—2·77: hardness very different in different parts; becomes colourless when heated; gives off water and melts before the blowpipe, swelling up to a white enamel. (Dana, ii. 234; Rammelsberg's Mineralchemie, 590.)

ANOTTO. See ANNOTTO.

ANOXOLUIN. According to Leconte and Goumoens (Compt. rend. xxxvi. 834), fibrin, muscular fibre, albumin, vitellin, globulin, and casein, contain two different substances, one of which, called *oxoluin*, dissolves in glacial acetic acid, while the other, *anoxoluin*, is insoluble in that acid. In fibrin and muscular fibre, the anoxoluin may also be distinguished, when examined by the microscope, by its fibrous structure, from the oxoluin, which is granular. Anoxoluin dissolves with reddish colour in dilute sulphuric acid, whereas oxoluin dissolves but sparingly and with yellowish colour. Anoxoluin is precipitated of a carmine-red colour by mercuroso-mercuric nitrate: oxoluin, light rose-red. Chromic acid dissolves anoxoluin at 100° C., forming a red-brown solution, whereas oxoluin is not affected by it. Hydrochloric acid dissolves the former readily, forming a violet solution, the latter but sparingly, with yellowish colour. A boiling saturated solution of tartaric acid dissolves anoxoluin readily, but not oxoluin.

ANTHOKIRRIN. The yellow colouring matter of the flowers of yellow toad-flax (*Linaria vulgaris* or *Antirrhinum Linaria*, L.).—It may be prepared by treating the flowers with warm alcohol, evaporating to dryness, exhausting with water to dissolve sugar, gum, &c., treating the insoluble portion with alcohol, evaporating again and digesting in ether. On evaporating the ethereal solution, the colouring matter is obtained in yellow nodules. It melts when heated, and sublimes apparently without decomposition. The fixed alkalis dissolve it with red colour; ammonia and alkaline carbonates, with dark yellow colour: from these solutions it is precipitated yellow by acids. Minerals acids dissolve it with red colour, the solutions becoming yellow on standing. The concentrated aqueous solution is precipitated reddish-yellow by acetate of lead, greenish-yellow by cupric-salts, orange-yellow by protochloride of tin. With hydrate of alumina it forms a pale yellow lake. The flowers of toad-flax are sometimes used for dyeing yellow; stuffs dyed with them have a light yellow colour, but assume a dirty yellow colour when exposed to the air. (Riegel, Pharm. Centralb. 1842, 454.)

ANTHOKYAN or **CYANIN.** The blue colouring matter of flowers. (See COLOURING MATTER.)

ANTHOLEUCIN. The white colouring matter of flowers. (See COLOURING MATTER.)

ANTHOPHYLLITE. A mineral belonging to the amphibole family. (See HORNBLENDE.)

ANTHOSIDERITE. A native silicate of iron, found at Antonio Pereira, in Minas Geraes, Brazil. It has an ochre-yellow colour inclining to yellow-brown, and a fibrous radiated structure. Its composition, according to Schnedermann's analysis, is $Si^9Fe^8O^{24} + 2H^2O = 2Fe^4O^3.9SiO^2 + 2H^2O$.

ANTHOXANTHIN. The yellow colouring matter of flowers. (See COLOURING MATTER.)

ANTHRACENE or **ANTHRACIN.** Syn. with PARANAPHTHALIN.

ANTHRACITE. *Blind coal*, *Kilkenny coal*, or *Glance coal*.—There are three varieties.—1. Massive, the conchoïdal of Jameson. Its colour is iron-black, sometimes tarnished on the surface, with a resplendent lustre. Fracture conchoïdal, with a pseudo-metallic lustre. It is brittle and light. It yields no flame, and leaves whitish ashes. It is found in the newest floetz-formations, at Meissner, in Hesse, and Walsall in Staffordshire.—2. *Slaty anthracite.* Colour black, or brownish-black. Imperfectly slaty in one direction, with a slight metallic lustre. Brittle. Specific gravity 1·4 to 1·8. Consumes without flame. It is composed of 72 carbon, 13 silica, 3·3 alumina, and 3·5 oxide of iron. It is found in both primitive and secondary rocks: at Calton Hill, Edinburgh; near Walsall, Staffordshire; in the southern parts of Brecknockshire, Carmarthenshire, and Pembrokeshire, whence it is called Welsh culm; near Cumnock and Kilmarnock, Ayrshire; and mostly abundantly at Kilkenny, Ireland.—3. *Columnar anthracite.* Small short prismatic concretions, of an iron-black colour, with a tarnished metallic lustre. It is brittle, soft, and light. It yields no flame or smoke. It forms a thick bed near Sanquhar in Dumfriesshire; at Saltcoats and New Cumnock in Ayrshire. It occurs also at Meissner in Hesse.—U. (See *Ure's Dictionary of Arts, Manufactures, and Mines.*)

ANTHRACOLITE or **ANTHRACONITE.** A variety of calc-spar or limestone, coloured black or blackish-brown, by coal and bituminous matter, occurring in certain aluminous schists, and similar formations containing vegetable and animal remains, as at Andreasberg in the Hartz, and at Christiania in Norway. When the bitumen predominates, the mineral is called *stinkstone*, from the property which it possesses of emitting, when rubbed or cracked, an odour like that of putrefying animal remains.

ANTHRACOXENE. A fossil resin which occurs in layers of great extent, and 2½ inches thick, between the strata of coal at Brandeisl, near Schlau in Bohemia. It is brownish-black in the mass, but exhibits a hyacinth-red colour in thin layers; has a shining surface, and conchoïdal fracture; is brittle, and yields a yellowish-brown powder. It melts and swells up strong when heated, and burns with a not unpleasant odour, leaving a residue of ferric oxide, lime, sulphuric acid, and silica. It appears to be a mixture of several substances. Ether dissolves a portion of it, leaving a resin, which has, according to Laurent, the composition $C^{40}H^{28}O^{18}$. The ethereal solution deposits after partial evaporation, a brown powder, containing $C^{40}H^{31}O^{7}$, and this, when exposed to the air, takes up oxygen, and becomes partially soluble in alcohol; and the alcoholic solution, precipitated with acetate of copper, yields a flocculent precipitate, containing oxide of copper, in combination with a resin, whose composition is expressed by the formula $C^{40}H^{30}O^{12}$. The portion left undissolved by the alcohol appears to contain $C^{40}H^{30}O^{8}$. (Handw. d. Chem. 2te Aufl. ii. 39.)

ANTHRANILIC ACID. See Phenylcarbamic Acid.

ANTHROPIN. Heintz, in examining human fat, obtained, besides stearic acid, an acid which melted at 52° C., and gave by analysis numbers corresponding to the formula $C^{17}H^{34}O^{2}$. This he at first supposed to be a peculiar acid (anthropic acid) existing in the fat in the form of a glyceride (anthropin); but later investigations proved that it was a mixture of stearic acid with margaric or palmitic acid. (Pogg. Ann. lxxxiv. 238; lxxxvii. 233.)

ANTIARIN, $C^{14}H^{20}O^{5} + 2H^{2}O$.—The poisonous principle of the *Upas antiar*, a kind of green resin which exudes from the upas tree (*Antiaris toxicaria*), and is employed by the Javanese for poisoning their arrows. It is extracted by exhausting the upas with boiling alcohol, evaporating to dryness after the antiar-resin (see below) has deposited, treating the extract with water, and evaporating to a syrup; the antiarin then takes the form of scales, which are purified by recrystallisation. It is without odour, dissolves at 22°·5 C. in 251 parts of water, 70 parts of alcohol, and 2·8 pts. of ether; the solution is neutral to test-papers. It likewise dissolves in dilute acids. When dried at ordinary temperatures, it contains 13·4 per cent of water of crystallisation, which it goes off at 112° C. It melts at 220° C. into a colourless liquid, which assumes a vitreous aspect on cooling, and at a higher temperature turns brown, and exhales acid vapours. Dehydrated antiarin contains $C^{14}H^{20}O^{5}$ (62·69 p.c. C and 7·45 H.) Sulphuric acid colours antiarin brown. Hydrochloric and nitric acids dissolve it without alteration; so likewise do potash and ammonia.

Antiarin applied to a wound produces vomiting, convulsions, diarrhœa, and soon afterwards death; its poisonous action is remarkably accelerated by mixture with a soluble substance, such as sugar. (Mulder, Ann. Ch. Pharm. xxviii. 304.)

ANTIAR RESIN, $C^{16}H^{24}O$.—The *upas antiar* also contains a resin which does not exhibit any poisonous action. It is extracted by treating the upas with boiling alcohol or ether, and is deposited on cooling in white, odourless, glutinous flakes, having a density of 1·032 at 20° C., melting at 60°; insoluble in water; soluble in 325 pts. of alcohol at 20°, and in 44 pts. of boiling alcohol. Boiling ether dissolves ⅝ pt. of the resin. It dissolves readily in essential oils, and is sparingly dissolved by caustic potash. Its alcholic solution is not precipitated by alcoholic acetate of lead; but on adding water to the mixture, a plastic mass is precipitated containing 23·44 per cent. oxide of lead. (Pelletier and Caventou, Ann. Ch. Phys. xxvi. 57; Mulder, Ann. Ch. Pharm. xxvii. 307.)

ANTICHLOR. The application of alkaline hypochlorites (chloride of lime, &c.) to the bleaching of cotton and linen, is attended with this inconvenience, that the fibre is apt to retain a quantity of free chlorine, which gradually rots and destroys it. Hence the necessity of removing this free chlorine, either by long continued washing, or by the application of some reagent which can unite with the chlorine, and convert it into an innocuous compound. Such reagents are called "Antichlors:" their use is especially necessary in the paper manufacture, in which long continued washing involves a considerable waste of the pulp, and on the other hand, the non-removal of the free chlorine is attended with a gradual rotting of the goods after stowage, fading of the coloured quantities, and in some instances partial obliteration of documents written upon the paper thus imperfectly prepared, besides injury of the delicate machinery of the manufactory.

The first substances used for this purpose were the neutral and acid sulphites of sodium (sulphite and bisulphite of soda). A patent for this application of the acid sulphite was granted in 1847 to Mr. Henry Donkin, a manufacturer of paper-maker's machinery, &c. at Bermondsey, and it was largely used till 1853, when it was superseded by *hyposulphite* of *sodium*, which is both cheaper to prepare and more efficacious, its practical value being just double that of the acid sulphite. (See Hyposulphites, under Sulphur.) The products formed by the action of chlorine, (or hypochlorous acid) on sulphite or hyposulphite of sodium, are sulphate and chloride of sodium, both of which are perfectly innocuous, and easily removed by washing.

To ensure the complete removal of the free chlorine, the bleached paper or other material, or the wash water which runs from it, must be tested with a mixture of iodide of potassium and starch: the slightest trace of chlorine will be indicated by a blue colour. To ascertain whether an excess of the antichlor has been used, add to the mixture of starch and iodide of potassium a few drops of the bleaching liquid, so as to produce a blue colour, and then add a portion of the liquid to be tested; if the antichlor is present in excess, the colour will be destroyed.

Sulphide of calcium, prepared by boiling sulphur with milk of lime, has also been used as an antichlor; so likewise has a solution of protochloride of tin in hydrochloric acid; in the latter case, however, it is necessary, after the completion of the bleaching process, to add carbonate of sodium, in order to neutralise the free hydrochloric acid, which would otherwise act as injuriously as the free chlorine itself. The precipitate of oxide of tin thereby produced is quite white and soft, and does not interfere with the subsequent stages of the paper manufacture.

Lastly, coal-gas has been used since 1818, as an antichlor in paper making; it does not appear, however, to be so convenient as the reagents above-mentioned. (See BLEACHING, *Ure's Dictionary of Arts, Manufactures, and Mines.*)

ANTICHLORISTIC THEORY. See CHLORINE.

ANTIGORITE. A hydrated silicate of magnesium belonging to the serpentine group, found in the valley of Antigoria in Switzerland. (See SERPENTINE.)

ANTIMONATES. See ANTIMONY, OXIDES OF.

ANTIMONIAL COPPER. Native sulphide of copper and antimony, or Wolfsbergite. (See COPPER, SULPHIDES OF.)

ANTIMONIAL COPPER GLANCE. Also called *Wolchite.*—A mineral found in the iron mines at St. Gertraud, in Carinthia. Short rhombic prisms with cleavage parallel to the brachydiagonal, imperfect; also massive. Specific gravity 5·7—5·8. Hardness = 3. Colour blackish lead-grey. Fracture conchoïdal, to uneven; brittle. Contains, according to Schrotter's analysis, 28·60 S, 16·5 Sb, 6·04 As, 29·50 Pb, 17·35 Cu, 0·40 Fe, = 95·94. (Dana, ii. 82.)

ANTIMONIAL CROCUS. See ANTIMONY, OXYSULPHIDE OF.

ANTIMONIAL LEAD ORES. See LEAD, SULPHIDES OF.

ANTIMONIAL NICKEL, and **ANTIMONIAL SILVER.** See ANTIMONY, ALLOYS OF.

ANTIMONIAL SULPHIDE of SILVER. See SILVER, SULPHIDE OF.

ANTIMONITE. Native Sulphide of Antimony.

ANTIMONITES. See ANTIMONY, OXIDES OF.

ANTIMONY. *Spiessglanzmetall, Spiessglassmetall, Antimoine, Antimonium, Stibium.* Symbol, Sb. Atomic weight (as determined by the recent experiments of Schneider) = 120·3.[*]

Some of the compounds of antimony were known to the ancients; but the method of preparing the metal itself was first described by Basilius Valentinus towards the end of the fifteenth century.

Antimony is found native, and alloyed with other metals; viz. with arsenic, nickel, and silver; also in combination with oxygen; viz. as trioxide, in the form of *antimony bloom, white antimony*, or *Valentinite*, Sb^2O^3 and as tetroxide, *antimony ochre*, or *Cervantite*, Sb^2O^4; in combination with sulphur, as *stibnite* or grey *antimony ore*, Sb^2S^3; with sulphur and oxygen, as *red antimony*, *antimony blende*, or *kermesite* $Sb^2O^3.2Sb^2S^3$; also as sulphide combined with various other metallic sulphides, chiefly those of lead and silver, *e.g. zinkenite*, $Pb^2S\ .\ Sb^2S^3$; *miargyrite*, $Ag^2S.Sb^2S^3$, &c. (See SULPHANTIMONITES.) Lastly it occurs in ferruginous water, associated with arsenic, tin, lead, and copper.

Preparation.—All the antimony of commerce is obtained from the native trisulphide, which occurs in many localities among the older rocks, gneiss, clayslate, porphyry, &c. The sulphide is first separated from its gangue by fusion (p. 329), then converted into oxide by roasting, and the oxide is subsequently reduced by coal or charcoal; or the sulphide is at once reduced to the metallic state by fusion with a mixture of charcoal and alkali, or with metallic iron. The following details are taken from Gmelin's Handbook, vol. iv. p. 318.

1. Powdered grey sulphide of antimony, mixed with about half its weight of charcoal powder to prevent caking, is roasted at a gentle heat (on the small scale, on a

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[*] Berzelius estimated the atomic weight of antimony at 129, which number was for a long time adopted; H. Rose (J. pr. Chem. lxviii. 115, 376) obtained the number 120·7; Dexter (Pogg. Ann. c. 563) estimated it at 122·3. (See page 321.)

roasting dish; on the large scale, in a reverberatory furnace), with constant stirring, the fire being gradually increased, but not sufficiently to fuse the mass. The sulphur escapes in the form of sulphurous acid, and there remains a mixture of tetroxide of antimony with a small quantity of trioxide, amounting to about $\frac{1}{3}$ of its weight (Geiger and Reimann, Mag. Pharm. xvii. 136), and traces of undecomposed sulphide of antimony: *Antimony-ash, Calx Antimonii grisea per se*, or *Cinis Antimonii*. This residue is then mixed with half its weight of cream of tartar, or with 1 part of charcoal and $\frac{1}{2}$ pt. potash, or with charcoal powder saturated with an aqueous solution of carbonate of sodium, and fused in a covered crucible at a low red heat; the fused mass is then poured out into a hot mould partly filled with tallow, and the mould gently tapped to make the metal sink to the bottom. The slag at the top consists of a mixture of alkaline carbonate, double sulphide of antimony and potassium (or sodium) and charcoal. The charcoal separates the oxygen from the antimony, and from a portion of the alkali; and the potassium or sodium thus eliminated separates the sulphur from part of the sulphide of antimony still present, and then, in the form of sulphide, unites with the remainder.—2. A mixture of 8 parts of sulphide of antimony, and 6 parts of cream of tartar is heated in a crucible, nearly to redness, and from 2 to 3 parts of nitre are added till the mass becomes perfectly fused. Or a mixture of 8 pts. of sulphide of antimony, 6 pts. of cream of tartar, and 3 pts. of nitre, is projected by small portions at a time into a red-hot crucible placed in a furnace, and the whole is heated for a short time, till perfectly fused. The mass is then poured out as before. The lower stratum consists of metallic antimony; the upper, of double sulphide of antimony and potassium mixed with charcoal. The charcoal in the black flux withdraws oxygen from the potash; the potassium thus separated decomposes a portion of the sulphide of antimony, setting the metal free; and the resulting sulphide of potassium unites with the still undecomposed sulphide of antimony. Probably according to the following equation:

$$6Sb^2S^3 + 6K^2O + 6C = 3(2K^2S.Sb^2S^3) + 4Sb + 6CO.$$

According to this, only $\frac{2}{5}$ of the antimony contained in the sulphide should be obtained in the metallic state, or from 100 parts of the sulphide of antimony, 29·15 parts of regulus. This result accords with actual experience, 100 parts of sulphide of antimony being found to yield 27 parts of antimony. According to Liebig, however, by leaving out the nitre in this process, 100 parts of sulphide of antimony produce 45 parts of the metal.—3. An intimate mixture of 8 parts of sulphide of antimony with 1 pt. of dry carbonate of sodium and 1 pt. of charcoal, heated in an earthen crucible, and constantly stirred with a stick till it fuses quietly, and then poured out into the casting mould, yields 5·7 parts (71 per cent.) of antimony, which is afterwards purified from iron and copper by fusion with $\frac{1}{4}$ its weight of nitre (Duflos, Br. Arch. xxxvi. 277; xxxviii. 158). In this process, rather more than 3 atoms of carbonate of sodium and charcoal are used to 1 atom of trisulphide of antimony, so that a sufficient quantity of sodium is set free to separate the whole of the sulphur:

$$Sb^2S^3 + 3Na^2O + 3C = 2Sb + 3Na^2S + 3CO.$$

The fusion must be continued for a long time, during which the mass is very apt to boil over, and the antimony to burn away; the total amount obtained is only 66 per cent., and the antimony still contains the whole of the other metals which were present in the sulphide (Liebig, Mag. Pharm. xxxv. 120).—4. A mixture of 177 pts. (1 at.) of sulphide of antimony with at most 82 pts. (3 at.) of iron filings or iron nails is heated to bright redness in a closely covered crucible, and then left to cool:

$$Sb^2S^3 + 6Fe = 2Sb + 3Fe^2S.$$

The iron separates the whole of the sulphur, even at a gentle heat; but a stronger heat is required to fuse the sulphide of iron, and cause the antimony to form a distinct stratum beneath it; at this high temperature, the antimony is apt to burn away if the crucible be not well covered; hence a layer of charcoal powder over the mixture is useful.—The addition of carbonate of potassium or sodium, or of nitre, accelerates the fusion, because double sulphide of iron and potassium or sodium is thereby formed, which is more readily fusible than pure sulphide of iron. For example, 22 pts. of nitre are added to a strongly ignited mixture of 100 pts. of sulphide of antimony and 33 pts. of iron, or 6 pts. of nitre to 100 pts. of sulphide of antimony and 47 pts. of iron; —or 100 pts. of sulphide of antimony, 43 pts. of iron, from 10 to 50 pts. of dry carbonate of sodium, and 2 to 5 pts. of charcoal are melted together. Berthier, however, found it most advantageous to fuse together 100 pts. of sulphide of antimony, 55—60 pts. of smithy scales, 45 pts. of carbonate of potassium, and 10 pts. of charcoal: this mixture yielded 69 pts. of antimony; the mass, however, was found to froth up considerably. Liebig (Mag. Pharm. xxxv. 120) gives the preference to this method; but the regulus which it separates from sulphide of antimony containing lead is contaminated with that metal (Ann. Ch. Pharm. xxii. 62). A mixture of 100 pts. of sulphide of antimony, 42 pts. of iron, 10 parts of dry sulphate of sodium, and 2½ pts. of charcoal, yields between 60 and 64 pts. of antimony (Liebig).—The slag obtained in the second process likewise yields a large quantity of antimony by fusion with iron, because the double sulphide of antimony and potassium is thereby converted into double sulphide of iron and potassium.

Antimony obtained by the first, second, and third processes,—the *Regulus Antimonii simplex s. vulgaris*, which solidifies in the mould, and has a stellated structure on the upper surface, whence it has been called *Regulus Antimonii stellatus*,—may contain sulphur, potassium, arsenic, lead, iron, and copper; the antimony prepared by the fourth method, *Regulus Antimonii martialis*, may contain a large quantity of iron, especially when the iron has been used in excess. The powdered antimony may be freed from iron by fusing it with sulphide of antimony; from sulphur, by fusion with carbonate of potassium; from sulphur and potassium, by fusion with nitre; and, according to Berzelius, from sulphur, potassium, arsenic, and iron, by fusion with from ½ to 1 pt. of antimonious oxide.

By fusing sulphide of antimony, or the slag obtained in the second process, with tin, lead, copper, silver, &c., an antimony is obtained, which may contain small quantities of these metals; antimony thus prepared was formerly called *Regulus Antimonii jovialis, saturninus, venereus, lunaris*, &c.

Purification.—1. By the following method, commercial antimony and likewise that prepared on the small scale, may be perfectly freed from sulphur, arsenic, iron (when not in too large quantity), and copper, but not from lead: hence the antimony subjected to this process, should be free from lead. A mixture of 16 pts. of coarsely pounded antimony with 1 pt. of grey sulphide of antimony and 2 pts. of dry carbonate of sodium, is fused in a hessian crucible for an hour, care being taken to prevent any charcoal from falling into the mass. When cold, the crucible is broken, and the slag completely separated from the metal, which is again coarsely pulverised, fused with 1½ pt. dry carbonate of sodium for an hour, and, lastly, after cooling and removal of the slag, once more fused with 1 pt. of carbonate of sodium. In this manner 15 pts. of pure antimony are obtained (Liebig, Ann. Ch. Pharm. xix. 22). The sulphide of antimony converts the other metals, except the lead, into metallic sulphides, which pass into the slag in combination with sulphide of sodium. The remaining arsenic is separated by the carbonate of sodium, in the form of arsenate of sodium. If any charcoal falls into the crucible, it reduces arsenic from the arsenate of sodium, whereby the antimony is again rendered impure (Liebig). Hence a black-lead crucible cannot be used; such a crucible also reduces sodium, which then mixes with the antimony (Anthon, Repert. lix. 240). If the commercial antimony has been prepared with iron, and is consequently richer in iron, a larger quantity of sulphide of antimony must be added in the first fusion, that is to say, in proportion nearly corresponding to the iron (4 pts. of sulphide of antimony and 4 pts. of carbonate of sodium, to 16 parts of the antimony): in this case, the loss of antimony is greater. As long as iron is present, it is impossible to remove the arsenic by means of carbonate of sodium (Liebig, Ann. Ch. Pharm. xxix. 58; Handwörterb. 2te Aufl. ii. 45; see also Buchner, Repert. li. 267).—2. Well washed powder of algaroth is reduced with alkali and charcoal. By this means, all impurities from the heavy metals are got rid of. Artus (J. pr. Chim. viii. 127) digests 1 pt. of finely powdered grey sulphide of antimony or glass of antimony, with 2 pts. of common salt, 3 pts. of oil of vitriol and 2 pts. of water for eight hours, then boils for one hour, and afterwards mixes the liquid with water till a permanent precipitate begins to appear; then filters; precipitates the powder of algaroth by adding more water; washes it thoroughly, and fuses 100 parts of the dry compound with 80 parts of dry carbonate of sodium and 20 pts. of charcoal-powder for fifteen or twenty minutes: 61 pts. of pure antimony are thus obtained.—3. A very pure metal may be obtained by heating tartrate of antimony and potassium (tartar-emetic) to bright redness, and digesting the resulting metallic mass in water, to remove any potassium that may have been reduced at the same time. (Capitaine, J. Pharm. xxv. 516; also J. pr. Chem. xviii. 449.)

Purification from Arsenic only.—The extensive use of antimonial preparations in medicine, renders the removal of this impurity a point of particular importance.—1. Four pts. of powdered commercial antimony are mixed with five pts. of nitre and 2 pts. of dry carbonate of sodium (without the latter, insoluble arsenate of antimony would be formed), and the mixture is projected into a red-hot crucible. The mass remaining after the combustion (which takes place quietly) is then pressed together, heated for half an hour to a higher temperature, so that it may become pasty but not fused, and pressed down as often as it swells up from evolution of gas. After this, it is taken out of the crucible with the spatula, while still hot and soft, then reduced to powder, and boiled for some time in water, with frequent stirring. The water, together with the finer powder, is then poured off; the coarser powder crushed with a pestle, and boiled with a fresh quantity of water; the two liquids with their deposits are mixed; and the insoluble portion is freed by repeated subsidence and decantation, and, lastly, by washing on a filter, from the alkaline solution which contains the alkaline arsenate and but a very small quantity of antimonate. The washed acid antimonate of potassium is white; but if it contains lead, which cannot be removed by nitric acid, it has a yellow colour. It is then fused with half its weight of cream of tartar at a moderate red heat, and the resulting metallic antimony containing potassium is pulverised and thrown into water, which removes the potassium and liberates pure hydrogen gas (Wöhler, Pogg. Ann. xxvii. 628; also Ann. Ch. Pharm. v. 20.) According to C. Meyer (Ann. Ch. Pharm. lxvi. 236; Centr. Blatt. 1348, 828) the use of nitre is objectionable, because it gives rise to the formation of antimonate of potassium, which destroys the exactness of the process. Meyer recommends a mixture of nitrate and carbonate of sodium, whereby a mass is obtained which does not yield a trace of antimony to water. This method is so exact that it may be used to separate antimony from arsenic in quantitative analysis; moreover, the antimony thus obtained is not contaminated with potassium or sodium. — 2. One part of pulverised antimony, prepared by the second method (p. 312), is rapidly fused with half its weight of carbonate of potassium, and the mass is poured out; the metal obtained is then crushed, fused with one-fourth its weight of nitre, again poured out, the metal again crushed, and fused with one-third its weight of hydrated antimonic acid; and lastly, the antimony, after being repulverised, is fused with one-third its weight of carbonate of potassium, and poured into the mould. This method completely removes the arsenic (Th. Martius, Kastn. Arch. xxiv. 253). — 3. If 32 pts. of antimony, rich in arsenic, are fused with 4 pts. of nitre, the slag contains a large quantity of arsenate of potassium; and the resulting 30 pts. of metal fused with 3 pts. of nitre, still yields a small quantity of arsenate of potassium and 27 pts. of metal; this, if again fused with 2 pts. of nitre, yields a slag containing scarcely anything but antimonate of potassium, and metallic antimony perfectly free from arsenic. If carbonate of potassium be used instead of nitre, the separation of the arsenic is much more difficult (J. A. Buchner, Repert. xliv. 246). — 4. One part of antimony prepared by the third method, is heated with 1½ pt. of oil of vitriol in a porcelain basin, stirring constantly as long as sulphurous acid gas continues to be evolved, and water is carefully added by small portions at a time, till a greyish-white intumescent mass is formed. This is then mixed in a vessel made of antimony, with from 0·2 to 0·4 pt. finely powdered fluor-spar, and 0·4 to 0·8 pt. oil of vitriol (according to the quantity of arsenic present). The whole is then heated, with constant stirring, as long as hydrofluoric acid and fluoride of arsenic are given off; the residue is afterwards gradually mixed with water, and washed by decantation till the wash-water ceases to exhibit an acid reaction; and the remaining basic sulphate of antimony is reduced by fusion with half its weight of cream of tartar, in a covered crucible. If a leaden vessel were used, antimony and arsenic would be reduced together, and consequently the antimony obtained would not be free from arsenic. (Duflos, Kastn. Arch. xix. 56; also, Schw. lx. 353; further, Schw. lxii. 501; see also Buchner and Herberger, Repert. xxxviii. 381, xliv. 246.)

Tests for Impurities in Antimony. — 1. *Sulphur.* The powdered metal, when heated with strong hydrochloric acid, gives off hydrosulphuric acid. — 2. *Potassium* or *Sodium.* The antimony appears more grey than white, and loses its lustre on exposure to the air. Its powder has an alkaline taste, reddens moist tumeric paper, and evolves hydrogen gas when put under water, giving up alkali to the liquid. — 3. *Arsenic.* The metal, when fused in the air, emits a garlic colour. If its powder be detonated with about ¼ pt. of nitre, and the resulting mass treated with water, a filtrate is obtained, which contains arsenate and antimonate of potassium, so that when supersaturated with hydrochloric acid, and rapidly saturated with hydrosulphuric acid gas, it first gives a yellowish red precipitate of pentasulphide of antimony, and then, if rapidly filtered and preserved in a close vessel, gradually deposits a yellow precipitate of pentasulphide of arsenic. The antimony ignited with an equal weight of cream of tartar in a covered crucible, yields an alloy of potassium, arsenic, and antimony, which, if reduced to powder under water, evolves arseniетted hydrogen, recognisable by its depositing brown metallic arsenic on ignition (see ARSENIC). — 4. *Lead.* The powdered metal boiled with nitric acid nearly to dryness, and then treated with water, yields a filtrate which contains nitrate of lead, and is consequently precipitated by sulphuric acid. When the quantity of lead is large, a solution of antimony in aqua-regia deposits crystalline needles of chloride of lead on cooling. — If the antimony contains sulphur besides the lead, the lead remains undissolved in the form of sulphate, on treating the metal with nitric acid. If the antimonious oxide in the residue is then dissolved out by warm hydrosulphate of ammonia, black sulphide of lead remains behind, and if iron is present, black sulphide of iron also.—5. *Iron.* The finely divided metal ignited with three times its weight of nitre, and washed with boiling water, leaves a yellowish residue, from which boiling dilute hydrochloric acid separates ferric oxide, which may be detected by ferrocyanide of potassium, &c.—6. *Copper.* When the lead has been precipitated from the nitric acid solution by sulphuric acid, according to the method above given, the cupric oxide remains dissolved, and may be recognised by its behaviour with hydrosulphuric acid, ferrocyanide of potassium, ammonia, or polished iron. A solution of antimony in aqua-regia should give a yellowish-red precipitate with sulphide of ammonium, perfectly soluble in excess of the precipitant. If a black residue is left, it must consist of sulphide of lead, iron, or copper. (H. Rose.)

Properties.—Antimony is a brilliant metal, having a bluish-white colour, and highly lamellated structure. By melting it in a crucible, then leaving it to cool partially, and pouring out the still liquid portion, it may be obtained in rhombohedral crystals. Its tendency to crystallise is well shown in the cakes of metal which are met with in commerce, the surface of which often exhibits beautiful stellate or fern-like markings. Its density is from 6·702 to 6·86. It is very brittle, and easily pulverised in a mortar. It melts at 450° C. (842° Fah.), and may be distilled at a white heat in an atmosphere of hydrogen, but the distillation is very slow, in consequence of the small density of the vapour. Metallic antimony occurs native in small quantity, sometimes in rhombohedral crystals, at Andreasberg in the Harz, at Przibram in Bohemia, at Sala in Sweden, and at Allemont in France.

Amorphous Antimony.—Antimony is deposited from its solutions by electrolysis in two different states. When thus precipitated, with a positive electrode of antimony, from a solution of 5 pts. of tartar emetic and 5 pts. of tartaric acid dissolved in a mixture of 2 pts. hydrochloric acid and 30 pts. water, it has a silvery-grey colour and frosted surface, is hard in texture, has a radiating crystalline structure, and a density of 6·55. But from a solution of 1 pt. of tartar emetic in 4 pts. of the ordinary chloride of antimony (containing excess of hydrochloric acid?) it is deposited with the colour and appearance of polished steel, and a bright, metallic, amorphous fracture. Its specific gravity is then only 5·78. This amorphous antimony, when heated or struck, undergoes a rapid and intense molecular change throughout its mass, attended with great evolution of heat (from 60° to upwards of 450° F.), increasing at the same time in density, and approaching in colour and structure to the crystalline variety. At the same time, a quantity of chloride of antimony and of gas, condensed within its pores and retained with considerable force, is given off. No such change takes place in the grey crystalline metal. By carefully triturating thin pieces of the amorphous metal under water, it may be obtained in the state of a fine powder, exhibiting the molecular property above mentioned. This change of antimony from the amorphous to the crystalline state appears to be similar to that which has been observed in sulphur, selenium, and other substances. (G. Gore, Proc. Roy. Soc. ix. 70.)

In a subsequent paper (Proc. Roy. Soc. ix. 304), Mr. Gore states that the evolution of heat accompanying the change "is not limited to a particular temperature, but commences between 170° and 190° F., and increases in rapidity to some point above 212° F., when it becomes sudden. The heat may be discharged either suddenly or gradually, according to the amount to be discharged relative to the cooling influences present. The specific heat of the unchanged (amorphous) metal was found to be 0·06312; and of the same specimens, after being gradually discharged, the specific heat was not sensibly different. But the specific heat of the substance, after sudden discharge, was found to be 0·0543. The total amount of heat evolved by the substance during the change was sufficient to raise the temperature of its own weight of ordinary antimony (specific heat = 0·0508) about 650 F." An acid solution of fluoride of antimony yielded by electro-deposition, crystalline antimony not possessing the heating powers.

Antimony is not sensibly altered by exposure to the air at common temperatures, but oxidises quickly when melted. At a red heat, it takes fire, burning with a white flame, and producing white fumes of the trioxide. A lump of the pure metal heated on charcoal before the blowpipe, burns brilliantly, emitting copious white inodorous vapours, and if left to cool before it is completely burnt away, becomes covered with a white network of the crystallised oxide. If, on the contrary, the antimony is contaminated with arsenic and iron, it exhales a garlic odour, especially at the commencement; becomes covered with a slag of oxide of iron; has a dull surface; ceases to burn as soon as the blowpipe flame is withdrawn; and yields a yellow oxide. (Liebig.)

Antimony is strongly attacked and oxidised by *nitric acid*, but not dissolved. The degree of oxidation varies with the strength of the acid. If the acid be moderately dilute, the product consists of trioxide of antimony, mixed with a small quantity of pentoxide; with strong nitric acid, on the contrary, the product consists chiefly or wholly of pentoxide (H. Rose, Analyt. Chem. i. 258). The metal is not acted upon by dilute *sulphuric acid*, but when heated with the strong acid, it is converted into sulphate, with evolution of sulphurous anhydride. In the state of fine powder, it is dissolved by boiling *hydrochloric acid*, with evolution of hydrogen, but in the compact state, it resists the action of that acid, even at the boiling heat.

Antimony forms, with acid or chlorous radicles, two classes of compounds, viz.

1. *Antimonious compounds* or *tri-compounds of antimony*, containing 1 atom of the metal with 3 atoms of a monobasic acid-radicle, Cl, Br, &c. or 2 atoms of metal with 3 atoms of a dibasic acid radicle, O, S, &c., *e. g.*:

Trichloride of antimony	$SbCl^3$
Trioxide or antimonious oxide	Sb^2O^3
Trisulphide	Sb^2S^3

2. *Antimonic compounds* or *penta-compounds of antimony*, in which 1 or 2 atoms of metal are associated with 5 atoms of an acid-radicle, *e. g.*:

Pentachloride of antimony	$SbCl^5$
Pentoxide or antimonic oxide	Sb^2O^5
Pentasulphide	Sb^2S^5

In the antimonious compounds, $Sb = H^3$; in the antimonic compounds, $Sb = H^5$.

There are likewise a few compounds of antimony not included in either of these series; *e. g.* the tetroxide, SbO^2, which may, however, be regarded as a compound of the two oxides above mentioned, viz. antimonoso-antimonic oxide, $Sb^2O^3.Sb^2O^5 = 4SbO^2$.

ANTIMONY, ALLOYS OF. Antimony unites with most of the heavy metals, rendering them harder and more brittle. Most of the alloys are easily formed by fusing the two metals together; some occur native. The alkali-metals likewise form alloys with antimony.

For the compounds of arsenic and antimony see ARSENIC.

Antimonide of Copper.—Prepared by fusing the two metals together in equal quantities is pale violet, very brittle, and of laminar texture. According to Karsten, copper alloyed with 0·15 per cent. of antimony, becomes somewhat cold-short and very hot-short.

Antimonide of Gold.—The two metals unite very easily, melted gold even absorbing vapour of antimony. An alloy of 9 pts. gold to 1 pt. antimony is very brittle, white, and exhibits the fracture of porcelain. Gold loses its malleability by admixture with about $\frac{1}{2000}$ of antimony. The antimony is easily expelled from the alloy by heat.

Antimonide of Iron.—A mixture of 7 pts. of antimony, and 3 pts. of iron heated to whiteness in a crucible lined with charcoal, forms a white, very hard, slightly magnetic alloy, which gives sparks when filed. An alloy of antimony and iron is always formed when sulphide of antimony is reduced by iron in excess (*regulus antimonii martialis*). A very small quantity of antimony (0·23 per cent.) makes refined iron both hot- and cold-short.

Antimonide of Lead.—The two metals unite readily in all proportions. Lead is hardened by admixture with antimony. An alloy of equal parts of the two is brittle and ringing; 12 pts. lead and 1 pt. antimony form a malleable alloy, somewhat harder than lead. *Type-metal* is an alloy of antimony and lead, usually containing 17 to 20 per cent. of antimony. Sometimes other metals are added, *e. g.* 1 pt. bismuth to 16 pts. lead and 2 pts. tin, or, for stereotype plates, $\frac{1}{80}$ to $\frac{1}{50}$ of tin. The specific gravity of alloys of lead and antimony is always above the mean.

Antimonide of Nickel, NiSb, occurs as a metallurgic product obtained by sublimation in long hexagonal prisms. Another alloy, Ni^2Sb, occurs as a natural mineral called *antimonial nickel* or *Breithauptite*, in thin hexagonal plates of specific gravity 7·541, hardness 5·5; fracture uneven; the recent fracture exhibits a light copper colour with a tinge of violet; powder red-brown. Not magnetic. Ignited in a glass tube, it yields a small sublimate of antimony. On charcoal it forms an antimonial deposit, and cannot be fused excepting in small pieces. It is but little attacked by simple acids, but dissolves easily in aqua-regia. Analysis by Stromeyer (Pogg. Ann. xxxi. 134):

Sb	Ni	Fe	Pb^2S	
63·73	28·95	0·87	6·44	= 99·99
59·71	27·05	0·84	12·36	= 99·96

It was formerly found in the Andreasberg mountains, with calc-spar, galena, and smaltine; but the vein has long been exhausted. A similar alloy may be obtained artificially by melting 2 at. Ni with 1 at. Sb. (Dana, ii. 53.)

Antimonide of Tin. — The alloy is easily formed by fusing the two metals together, also by reducing sulphide of antimony with tin (*regulus antimonii jovialis*). Britannia metal is an alloy of 9 pts. tin and 1 pt. antimony, frequently also containing small quantities of other metals, as copper, zinc, and bismuth. Alloys of antimony with tin, or tin and lead, sometimes also containing copper, are now much used for machinery bearings in place of gun-metal. (See *Ure's Dictionary of Arts, Manufactures, and Mines*, i. 169.)

Antimonide of Zinc. — Antimony forms with zinc, alloys of definite crystalline character. A fused mixture of the two metals, containing from 43 to 70 per cent. of zinc, deposits by partial cooling, silver-white rhombic prisms, containing from 43 to 64 per cent. of zinc. The alloy containing exactly 43 per cent. of zinc, appears to be a definite compound, *stibiotrizincyl*, $SbZn^3$. Mixtures containing from 33 to 20 per cent. of zinc deposit rhombic crystals containing from 35 to 21 per cent. of zinc. The alloy containing exactly 33 per cent. is *stibiodizincyl*, $SbZn^2$. These alloys, especially $SbZn^3$, decompose water, with evolution of hydrogen at the boiling heat, and very rapidly under the influence of acids. (J. P. Cooke, Sill. Am. J. [2] xviii. 229; xx. 222.)

Antimonide of Potassium. — Alloys of antimony and potassium may be obtained by fusing the two metals together, or by igniting metallic antimony, or its oxide or sulphide, with an organic salt of potassium. Thus, when 5 pts. of crude tartar and 4 pts. of antimony are slowly heated in a covered crucible till the mixture becomes charred, then heated to whiteness for an hour, and left to cool, a crystalline regulus is obtained containing 12 per cent. of potassium. This alloy decomposes water rapidly, and oxidises slowly in the air when in the compact state, but becomes heated and takes fire when rubbed to powder. (Löwig and Schweizer.)

Antimonide of Silver. — Ag^4Sb and Ag^6Sb occurs native as *antimonial silver* or *discrasite*, in the form of six-sided prisms with truncated lateral edges; also in scalenohedrons, similar to those of calc-spar. Specific gravity 9·4 to 9·8; hardness 3·5 to 4; silver-white; fracture uneven. Before the blowpipe, it gives off fumes of antimony, and leaves a grey, non-malleable, metallic globule; by continuing the heat on charcoal, silver is obtained. It dissolves in nitric acid, leaving oxide of antimony. Analysis by Klaproth:

	Ag^4Sb		Ag^6Sb
	a.	*b.*	*c.*
Antimony . . .	24	24	16
Silver . . .	76	76	84
	100	100	100

a is a coarse-grained variety from Wolfach, in Baden; *b* lamino-granular, from Andreasberg, in the Hartz; *c* fine-grained, from Wolfach. The mineral occurs also at Wittichen, in Suabia; at Allemont, in Dauphiné; at Casalla, in Spain; and near Coquimbo, South America. (Gm. vi. 199; Dana, ii. 35.)

Antimonide of Sodium resembles antimonide of potassium, and is prepared in like manner.

ANTIMONY BLOOM. Native trioxide of antimony.

ANTIMONY, BROMIDE OF. $SbBr^3$.—This is the only known compound of antimony and bromine, and is formed by direct combination. Antimony takes fire in bromine vapour, or in contact with liquid bromine, running about on the surface in melted globules. To prepare the compound, bromine is put into a retort, and dry antimony powder is introduced through the tubulus, agitating each time till the combination is complete. The product is then purified by distillation. It forms on cooling a mass of colourless needles, deliquescent, melting at 90°C., volatile at 270°. Water decomposes it, forming an oxibromide.

ANTIMONY, CHLORIDES OF. Antimony and chlorine unite directly when brought in contact, and if the antimony is in a state of fine division, the combination is attended with visible combustion. The compound formed is a trichloride or a pentachloride, according as the antimony or the chlorine is in excess.

TRICHLORIDE OF ANTIMONY, $SbCl^3$, is obtained:—1. By passing chlorine gas slowly through a tube containing excess of antimony, or over heated trisulphide of antimony, the chloride of sulphur formed at the same time being afterwards volatilised by a gentle heat. - 2. By distilling 3 pts. of antimony with 8 pts. of mercuric chloride, or 2 pts. of the trisulphide of antimony with 4·6 pts. of mercuric chloride:

$$Sb + 3HgCl = SbCl^3 + 3Hg;\ \text{and}\ Sb^2S^3 + 6HgCl = 2SbCl^3 + 3Hg^2S.$$

3. By heating the trisulphide with strong hydrochloric acid, or metallic antimony with hydrochloric acid to which nitric acid is added in successive small portions: if too much nitric acid were added, a precipitate of oxide of antimony or antimonic acid would be formed. A solution of the trichloride in excess of hydrochloric acid is thus formed, and on subsequently distilling this liquid, water and hydrochloric acid pass over first, and afterwards the pure trichloride.

Trichloride of antimony is at ordinary temperatures a translucent fatty mass—thence called butter of antimony. It melts at 72° C., and boils at about 200°: fumes slightly in the air, and is very corrosive. When thrown into water, it is decomposed into hydrochloric acid and trioxide of antimony, which however remains united with a portion of the chloride, forming a white powder called *powder of algaroth*. The same decomposition takes place on adding water to the solution of the trichloride in strong hydrochloric acid. The precipitate is redissolved by excess of hydrochloric acid, and the solution, which contains hydrated trichloride of antimony, is the most convenient that can be used for exhibiting the reactions of antimony. The addition of tartaric acid to this solution, prevents its decomposition by water.

The anhydrous trichloride combines with ammonia, forming the compound $NH^3.SbCl^3$, and forms crystalline compounds with the chlorides of the alkali-metals.

PENTACHLORIDE OF ANTIMONY, $SbCl^5$, is formed, with brilliant combustion, when finely powdered antimony is thrown into chlorine gas. It may be prepared by passing dry chlorine over pulverised antimony, gently heated in a tubulated retort provided with a receiver, or over the trichloride. Hofmann (Chem. Soc. Qu. J. xiii. 65) introduces metallic antimony coarsely powdered into a combustion-tube five or six feet long, rising at an angle of 10° or 15°, one end being fitted into a tubulature of a two-necked glass globe, the other neck of which is connected with a tube supplying dry chlorine. Combination takes place in the tube, and the products flow backwards into the globe, whilst the long layer of antimony prevents the escape of any chlorine.—Pentachloride of antimony is a colourless or yellowish, very volatile liquid, which emits suffocating vapours. *Water* first converts it into a crystalline hydrate and then decomposes it, forming hydrochloric and antimonic acids. It absorbs *ammonia* and *phosphoretted hydrogen*, forming solid red-brown compounds. It absorbs *olefiant gas*, C^2H^4, as readily as chlorine, and forms Dutch liquid. By passing dry olefiant gas and dry chlorine simultaneously through boiling pentachloride of antimony, in a retort connected with an inverted condenser, large quantities of Dutch liquid may be easily obtained. The pentachloride here acts as a carrier of free chlorine, a purpose for which it may often be advantageously used (Hofmann, *loc. cit.*) It likewise absorbs *hydrosulphuric acid gas*, at ordinary temperatures, forming a white crystalline chlorosulphide of antimony, $SbCl^3S$, analogous to chlorosulphide of phosphorus, PCl^3S.—With *bisulphide of carbon*, the latter being in excess, it yields tetrachloride of carbon, trichloride of antimony, and free sulphur:

$$CS^2 + 2SbCl^5 = CCl^4 + 2SbCl^3 + S^2.$$

The mixture becomes very hot, and on cooling deposits crystals of trichloride of antimony, mixed with sulphur-crystals, the tetrachloride of carbon remaining in the liquid state (Hofmann, *loc. cit.*). The pentachloride combines with *hydrocyanic acid*, forming a white, crystalline, volatile compound, containing $SbCl^5.3HCy$: also with *chloride of cyanogen*.—A white pulverulent substance containing $2SbCl^5.3SCl^2$, is obtained by heating pentasulphide of antimony in dry chlorine gas; it is decomposed at 300° C. into chloride of sulphur, trichloride of antimony, and free chlorine.

ANTIMONY, DETECTION AND ESTIMATION OF:

1. *Blowpipe Reactions.*—Solid compounds of antimony fused upon charcoal, with dry carbonate of sodium or cyanide of potassium, yield a brittle globule of antimony, a thick white fume being at the same time given off, and the charcoal covered to some distance around with a white deposit of oxide. If the heat be continued for some time, the globule will be completely dissipated. The reduction with cyanide of potassium may be performed in a porcelain crucible without charcoal.

The antimony globule is converted by nitric acid into a white oxide, soluble in a boiling solution of cream of tartar. It is insoluble in pure hydrochloric acid, but dissolves easily on addition of a small quantity of nitric acid, forming a solution of the trichloride, which is decomposed by water, forming a white precipitate, soluble in excess of hydrochloric or tartaric acid. If tartaric acid be previously added, water produces no precipitate.

2. *Liquid Reactions.*—The acid solution of the trichloride gives with *hydrosulphuric acid gas*, a brick-red precipitate of the trisulphide, easily soluble in sulphide of ammonium, and reprecipitated by acids.—With *potash*, it forms a white precipitate of the trioxide, soluble in a large excess of the reagent.—*Ammonia* forms the same precipitate, insoluble in excess. *Carbonate of potassium* or *sodium* also gives a white precipitate of the trioxide, which dissolves in excess, especially of the potassium-salt, but reappears after a while. If, however, the solution contains *tartaric acid*, the precipitate formed by potash dissolves easily in excess of the alkali,—ammonia forms but a slight precipitate, and only after long standing,—and the precipitates formed by the alkaline carbonates are insoluble in excess of those reagents. These last mentioned characters are also exhibited by a solution of tartar-emetic (tartrate of antimony and potassium). The solution of this salt is decomposed by the stronger acids, yielding a white precipitate, consisting of acid tartrate of potassium, mixed with the oxide or a basic salt of antimony. With solutions of barium, strontium, calcium, lead, and silver, it forms white precipitates, consisting of tartar-emetic, the potassium of which is replaced by the other metal.

A solution of *trichloride of gold*, added to a solution of trichloride of antimony, or other antimonious salt, forms a yellow precipitate of metallic gold, antimonic acid being at the same time precipitated in the form of a white powder, unless the solution contains a larger excess of hydrochloric acid:

$$4AuCl^3 + 3Sb^2O^3 + 6H^2O = 4Au + 12ClH + 3Sb^2O^5.$$

The reduction is slow at ordinary temperatures, but is accelerated by heating. In a solution of the trioxide (antimonious acid), in potash, trichloride of gold produces a black precipitate, which affords a very delicate reaction for antimonious acid. *Nitrate of silver* produces in a solution of trichloride of antimony, a white precipitate, from which ammonia dissolves out chloride of silver, leaving oxide of antimony undissolved. In a solution of antimonious acid in potash, nitrate of silver produces a deep black precipitate, insoluble in ammonia. In a solution of tartar-emetic, nitrate of silver forms a white precipitate, perfectly soluble in ammonia: but if the solution be previously mixed with excess of potash, nitrate of silver produces a black precipitate insoluble in ammonia.

Zinc and *iron* precipitate antimony from its solutions, in the form of a black powder.—*Copper* precipitates it in the form of a brilliant metallic film, which may be dissolved off by a solution of permanganate of potassium, yielding a solution which will give the characteristic red precipitate with hydrosulphuric acid. (Odling, Guy's Hospital Reports [3] ii. 249.)

Antimonic Acid is distinguished from antimonious acid by the different colour of the precipitate which it forms with *hydrosulphuric acid* (p. 328); but better by its behaviour with chloride of gold and nitrate of silver. *Trichloride of gold* produces no precipitate in solutions of antimonic acid, not even when they contain excess of potash. *Nitrate of silver*, added to a solution of antimonate of potassium, forms a white precipitate of antimonate of silver, perfectly soluble in ammonia: if the solution contains excess of potash, the precipitate is brown from admixed oxide of silver, but even then it is completely soluble in ammonia. The slightest trace of antimonious acid present produces a black precipitate, insoluble in ammonia. If a small quantity of an oxide of antimony in the solid state be rubbed up with water to a milky liquid in a porcelain capsule, then dried, and moistened with *ammonio-nitrate of silver*, a black spot will be produced, if trioxide antimony is present, either in the free state or combined with antimonic acid: but if only antimonic acid is present, no blackening will take place. This is a very delicate reaction (Bunsen, Ann. Ch. Pharm. cvi. 1).—Antimonic acid may also be distinguished from the trioxide by its behaviour with *hydriodic acid*, The pure trioxide dissolves in hydrochloric acid to which iodide of potassium is added, producing a pale yellow liquid, containing tri-iodide of antimony, without separation of iodine; but antimonic acid or antimonate of antimony, forms under the same circumstances a solution coloured dark brown by free iodine:

$$Sb^2O^3 + 6HI = 2SbI^3 + 3H^2O$$

and

$$Sb^2O^5 + 10HI = 2SbI^3 + 5H^2O + 4I.$$

If the quantity of antimonic acid is considerable, the liquid gives off violet vapours on boiling; but even if it does not exceed a few hundredths of a milligramme, the free iodine in the solution may be detected by shaking it up with a few drops of bisulphide of carbon, which then exhibits a violet or amethyst colour when it rises to the surface. It is of course essential that the hydrochloric acid do not contain free chlorine, and that the iodide of potassium be free from iodate. (Bunsen.)

When the presence of antimony is suspected in liquids containing considerable quantities of organic matter, as in cases of supposed poisoning by tartar-emetic or other antimonial preparations, it is best to destroy the organic matter by oxidation with hypochlorous acid. If the matter to be examined is solid, it should be cut into small pieces; if a large quantity of liquid is present, it must be brought by evaporation to a convenient bulk. It is then mixed with strong hydrochloric acid, a gentle heat applied, and chlorate of potassium added by small portions, till the liquid acquires a light yellow colour. It is then heated till the odour of chlorine is no longer perceptible, and afterwards left to cool and filtered. From the clear liquid thus obtained, the antimony may be precipitated by hydrosulphuric acid, or by metallic copper, and the precipitates treated in the manner already described; or the liquid may be introduced into a Marsh's apparatus (see ARSENIC), with zinc and dilute sulphuric acid, and the antimony reduced, either in the escape-tube by the heat of a lamp, or on a porcelain plate held in the flame. The metallic deposit thus obtained may be dissolved in aqua-regia, and the solution treated with hydrosulphuric acid, which will produce the characteristic brick-red precipitate. Another method of testing the deposit is to moisten it with nitric acid, of specific gravity 1·42, then heat the vessel over a lamp, and blow over the surface so as to cause the acid to evaporate without boiling. The white deposit then remaining consists chiefly or wholly of trioxide of antimony, which will produce a deep black spot with ammonio-nitrate of silver. A deposit of metallic arsenic, treated in the same way, gives with ammonio-nitrate of silver, either a yellow precipitate of arsenite, or a red-brown precipitate of arsenate of silver, according to the degree of oxidation produced by the nitric acid. (Bunsen.)

3. *Quantitative Estimation.*—1. Antimony may be accurately estimated in the form of tetroxide or antimonate of antimony, SbO^2, that oxide being neither volatile nor decomposible at a red heat. The antimony being precipitated from solution by hydrosulphuric acid, the precipitate is washed and dried, then placed, together with the filter, in a porcelain basin covered with a funnel, and fuming nitric acid poured upon it. A violent action then takes place, the antimony and the greater part of the sulphur being immediately oxidised: the oxidation of the sulphur may be completed by heating the vessel over a water-bath. The resulting white mass, consisting of antimonic acid mixed with sulphuric acid, is converted by ignition into pure antimonate of antimony, containing 79·22 per cent. of the metal. The oxidation of the sulphide of antimony cannot be conveniently effected by nitric acid of ordinary strength (specific gravity 1·42), because that liquid boils at a temperature 10° C. above the melting point of sulphur, and consequently the sulphur separated at the commencement of the action collects in melted globules, which are extremely difficult to oxidise, and if left in the mass during the subsequent ignition, would reconvert a portion of the oxide of antimony into sulphide. Fuming nitric acid, on the contrary, boils below the melting point of sulphur, and the sulphur separated by its action takes the form of a fine powder, which is easily oxidised at a gentle heat. If the sulphide of antimony is mixed with a large quantity of free sulphur (which is often the case when it has been dissolved in an alkaline sulphide and reprecipitated by an acid), it is best to remove the free sulphur by washing the precipitate with bisulphide of carbon.

The oxidation of the sulphide of antimony may also be effected by igniting it with mercuric oxide (prepared by precipitating a hot solution of mercuric chloride with excess of caustic potash). When these substances are heated together in equivalent proportions, a violent explosion takes place; but if the sulphide of antimony be mixed with between thirty and fifty times its weight of mercuric oxide, the oxidation takes place quietly. The mixture is heated in a porcelain crucible, gently, so long as mercurial vapours go off, afterwards more strongly, and at last very strongly, to expel the last traces of mercury. Antimonate of antimony then remains in the form of a soft white powder. As mercuric oxide, even when prepared with the greatest care, always leaves a small residue when ignited, the amount of this residue must be determined once for all, and the proportionate amount deducted from the weight of the antimonate of antimony. As, however, this residue never exceeds a few thousandths of the whole, it is not necessary to weigh the oxide of mercury with great exactness. In this process, it is necessary, if the sulphide of antimony contains a large excess of free sulphur, to remove that substance by washing with bisulphide of carbon, before proceeding to the ignition; because free sulphur, even when ignited with a large excess of mercuric oxide, produces explosions which might occasion loss. The method just described has been lately introduced by Bunsen (Ann. Ch. Pharm. cvi. 3). It is quite exact, provided due attention be paid to the precautions above indicated.

2. The precipitated sulphide of antimony is collected on a weighed filter, dried in an oil-bath, at about 120° C., and then weighed. A known portion of it is then either decomposed by ignition in an atmosphere of hydrogen, whereby the sulphur is expelled

in the form of hydrosulphuric acid, and metallic antimony remains: or a weighed portion of the sulphide is oxidised by means of hydrochloric acid and chlorate of potassium, the action being continued till the greater part of the sulphur is converted into sulphuric acid, and the remainder collected at the bottom of the liquid in a melted globule. The liquid is then diluted with water containing tartaric acid, to prevent the precipitation of a basic salt of antimony, and decanted; the globule of sulphur washed and weighed, and the quantity of sulphur in solution estimated as sulphate of barium (see SULPHUR), the quantity thus found being added to the weight of the globule. The proportion of sulphur in the precipitated sulphide of antimony being thus found, the amount of antimony is easily calculated. Antimony cannot be accurately estimated by merely weighing the precipitated sulphide, because the precipitate almost always contains free sulphur, and sometimes pentasulphide of antimony in unknown proportion.

When antimonious and antimonic acids exist together in solution, the total quantity of antimony may be estimated by treating one portion of the liquid as above described, and the quantity existing as antimonious acid determined in another portion by means of trichloride of gold, 4 at. of precipitated gold corresponding to 3 at. of antimony (p. 313).

Atomic Weight of Antimony.—**Berzelius** (Schw. J. xxii. 69) determined the amount of tetroxide produced from a given weight of the metal by oxidation with nitric acid, and thence found, for the atomic weight of antimony, the number 129·03. The same process has more recently been followed by **Dexter** (Pogg. Ann. c. 579), who found the smaller number 122·33: but even this number is generally regarded as too high, the error being supposed to arise from incomplete oxidation and the consequent admixture of trioxide with the tetroxide.

The number at present most generally adopted is that determined by **Schneider** (Pogg. Ann. xcviii. 293) from the analysis of the native trisulphide by hydrogen. Stibnite from Arnsberg, which consists of pure trisulphide of antimony mixed with only a small quantity of quartz (about ½ per cent.), was decomposed by ignition in a stream of hydrogen, and the reduced antimony weighed, the escaping gas being passed into aqueous ammonia to absorb any sulphide of antimony that volatilised, and this quantity being afterwards precipitated by hydrochloric acid, oxidised by fuming nitric acid, and weighed as tetroxide (its quantity did not exceed 1 or 2 milligrammes). Corrections were also made for the quartz in the mineral and for the small amount of sulphide which remained unreduced and unvolatilised; for which purpose the residue in the reduction-tube was weighed,—then digested in aqua-regia, the residual quartz again weighed, the sulphur in the solution determined by precipitation as sulphate of barium, and the amount of antimony in the residue thence determined (about 0·4 per cent.) After making these corrections, the composition of the trisulphide (Sb^2S^3) was found to be 71·480 Sb + 28·520 S = 100, whence, the atomic weight of sulphur being 32, that of antimony is:

$$Sb = \frac{71{\cdot}48}{28{\cdot}52} \times 48 = 120{\cdot}30.$$

This result agrees nearly with former determinations by H. Rose, and also with that found by **Weber** (Pogg. Ann. xcviii. 455), from the analysis of trichloride of antimony, viz. 120·7. Dumas, by decomposing trichloride of antimony with a standard solution of silver, finds for the atomic weight of antimony the number 122. (Ann. Ch. Pharm. cxiii. 29.)

Valuation of Antimony Ores.—To estimate the amount of antimony in the native sulphide, the ore is carefully roasted, and then fused at a moderate heat with 1 to 3 pts. of black flux and about 25 per cent. of borax, the whole being covered with a layer of common salt. The quantity of metal which can be thus extracted from the sulphide does not exceed 54 to 64 per cent, the calculated quantity being 71·5 per cent. Or the sulphide is fused with iron filings (about 42 pts. iron to 100 of sulphide), together with three times its weight of black flux, and about 25 per cent. of borax, the whole being covered with a thick layer of common salt. This process yields 66 to 68 antimony from 100 pts. of the sulphide.

To estimate the amount of sulphide of antimony in a sample of the crude ore, the ore, in pieces of about the size of a walnut, is heated in a hessian crucible perforated at bottom, and standing on another crucible placed below the grate, and surrounded with ashes or sand to keep it cool. Care must be taken to avoid applying too much heat.

If the gangue is not attacked by hydrochloric acid, the amount of sulphide may be estimated by boiling a weighed portion of the ore with that acid and weighing the residue. (**Kerl**, Hüttenkunde, iii. 26.)

4. *Separation of Antimony from other metals.*—From the metals of the second and third groups (see ANALYSIS, p. 213) antimony is separated by precipitation

with hydrosulphuric acid; from those of the first group, whose sulphides are insoluble in alkaline sulphides, it is separated by precipitating with hydrosulphuric acid and digesting the precipitate in sulphide of ammonium. The sulphide of antimony then dissolves, the other metals remaining undissolved; and on mixing the filtrate with excess of hydrochloric or acetic acid, the sulphide of antimony is reprecipitated. When hydrochloric acid is used, care must be taken to keep the liquid dilute and not allow it to get hot, otherwise some of the antimony may be redissolved.

When antimony is combined with other metals in the form of an alloy, it may often be separated by treating the alloy with moderately strong nitric acid, which dissolves the other metals, leaving the antimony in the form of antimonic acid, which may then be converted into antimonate of antimony by ignition. This method, however, is not rigidly exact, because the nitric acid dissolves a small portion of the antimony; but it is near enough for commercial purposes. It is of course not applicable to the separation of antimony from tin, gold, or platinum.

The separation of antimony from *tin* may be effected by immersing in the solution a piece of pure tin, which precipitates the antimony in the form of a black powder. To render the separation complete, a gentle heat must be applied, and the solution should contain an excess of acid. The antimony is collected on a weighed filter, dried at a gentle heat, and weighed. If the sum of the weights of the two metals in the solution is previously known, the amount of tin is at once determined by difference; if not, the metals must be precipitated together by zinc from a known quantity of the solution, and the antimony precipitated by tin from another portion.—Another method of separation given by Levol (Ann. Ch. Phys. [3] xiii. 125) is, to precipitate the two metals by zinc, and treat the precipitate with strong hydrochloric acid, without previously decanting the solution of chloride of zinc. The tin then dissolves, while the antimony remains undissolved, the presence of the chloride of zinc diminishing its tendency to dissolve in the acid. The tin may be afterwards precipitated by hydrosulphuric acid, and the sulphide converted into stannic oxide by treating it with strong nitric acid.

For the separation of antimony from *arsenic*, *gold*, and *platinum*, see those metals. From *selenium* and *tellurium*, antimony is separated in the same manner as arsenic (*q. v.*)

ANTIMONY, FLUORIDE OF. SbF^3.—Obtained by dissolving the trioxide in hydrofluoric acid. It forms colourless crystals, which dissolve completely in water without decomposition.

ANTIMONY, GLASS OF. See ANTIMONY, OXYSULPHIDE OF.

ANTIMONY, HYDRIDE OF, or **ANTIMONIDE OF HYDROGEN,** generally called *Antimonetted* or *Antimoniuretted hydrogen* SbH^3.—When an antimony-compound, tartar-emetic for example, is introduced into an apparatus in which hydrogen is generated by the action of zinc or dilute sulphuric acid, the flame produced by the combustion of the gas at the orifice of the jet, acquires a bluish tinge from admixture of antimonide of hydrogen. This compound may be obtained in a state of greater purity by dissolving an alloy of 2 pts. of zinc and 1 pt. of antimony in hydrochloric or dilute sulphuric acid. It is always, however, more or less contaminated with free hydrogen.

It is a colourless gas, and when free from arsenic, quite inodorous; insoluble in water and in alkaline liquids. When it is passed into hot concentrated nitric acid, a white powder is deposited, consisting of antimonic acid. When passed into a solution of nitrate of silver or chloride of mercury, it forms a black precipitate, containing the whole of the silver or mercury. The silver-precipitate has been found to be $SbAg^3$, and is formed by simple substitution of silver for hydrogen. Hence the antimonide of hydrogen is inferred to be SbH^3, analogous to ammonia, and to arsenide and phosphide of hydrogen, AsH^3 and PH^3.

When antimonide of hydrogen is passed through a tube of hard glass and strongly heated by the flame of a lamp, it is decomposed, and a mirror of metallic antimony is deposited on the tube. If a funnel be held over the flame of the gas, a deposit of trioxide of antimony is formed on its inner surface. A cold porcelain dish held in the middle of the flame, becomes covered with spots of metallic antimony, which are darker in colour than those formed in a similar manner by arsenic, and are further distinguished from the latter by not dissolving in hypochlorite of sodium. The antimony deposit dissolves easily in aqua-regia and in permanganate of potassium, and the solution thus formed exhibits the characteristic reactions of antimony with hydrosulphuric acid, &c. (p. 319).

There are several compounds of antimony with alcohol-radicles, analogous to antimonetted hydrogen, viz. *stibtrimethyl*, $Sb(CH^3)^3$, *stibtriethyl*, $Sb(C^2H^5)^3$, and *stibtriamyl*, $Sb(C^5H^{11})^3$.

ANTIMONY, IODIDE OF. SbI^3.—Prepared like the bromide. It is a dark red body, decomposed by water, forming an *oxyiodide*. The *sulphiodide*, $Sb^2I^2S^3$, is obtained as a red sublimate, by heating an intimate mixture of iodine and the trisulphide in a retort. It is decomposed by water, yielding hydriodic acid and an oxysulphide.

ANTIMONY, ORES OF. See p. 311; for the valuation, p. 321.

ANTIMONY, OXIDES OF. Antimony forms with oxygen three definite compounds, viz.: the

Trioxide or Antimonious oxide	Sb^2O^3 or SbO^3
Tetroxide or Antimonoso-antimonic oxide . . .	Sb^2O^4 or SbO^4
Pentoxide or Antimonic oxide	Sb^2O^5 or SbO^5

The tetroxide is perhaps a compound of the other two, $Sb^2O^3.Sb^2O^5 = 2Sb^2O^4$. A *suboxide* Sb^2O (?) is also said to be produced, as a grey film, when antimony is used as the positive pole in the electrolysis of water. It appears, however, to be merely a mixture of the metal with the trioxide, for, when treated with hydrochloric acid, it yields solution of the trioxide and a residue of antimony. (Berzelius.)

TRIOXIDE OF ANTIMONY, or ANTIMONIOUS OXIDE, Sb^2O^3, occurs, though rarely, as a natural mineral (*Valentinite, White Antimony, Antimony-bloom, Weisspiessglanzerz*), in shining white crystals belonging to the trimetric system; specific gravity 5·566 hardness; 2·5—3. It occurs in veins of primary rocks at Przibram in Bohemia, at Bräunsdorf in Saxony, and at Malaczka in Hungary. It is found also in regular octahedrons, viz. as *Senarmontite*, a mineral from the Gued Hamimim mine, in the province of Constantine, Algeria: it is therefore dimorphous. This oxide is formed when the metal burns in the air, and may be prepared by heating antimony in a crucible imperfectly closed with its cover: it is then deposited on the sides of the crucible, a little above the melted metal, in shining prismatic crystals, known by the name of *flowers of antimony, flores antimonti argentei*. But the easiest mode of obtaining it is, to heat the trisulphide with strong hydrochloric acid as long as hydrosulphuric acid continues to escape, and pour the resulting solution of the trichloride into a boiling solution of carbonate of sodium. A crystalline powder is then deposited, consisting (according to Graham) of the anhydrous trioxide:

$$2SbCl^3 + 3Na^2CO^3 = Sb^2O^3 + 6NaCl + 3CO^2.$$

Regnault, however, states (Cours de Chimie, iii. 239) that the oxide thus obtained is a hydrate, containing $Sb^2O^3.H^2O$ or $SbHO^2$. The trioxide is likewise obtained, though mixed more or less with antimonic acid, by treating metallic antimony with nitric acid (p. 318).

The artificial as well as the native trioxide of antimony is dimorphous. The crystals produced by the rapid oxidation of the metal belong to the trimetric or right prismatic system. Sometimes, however, when the oxide is sublimed at a comparatively low temperature, as when a few ounces of antimony are heated till the metal begins to burn, and then left to cool slowly, the prismatic crystals are mixed with regular octahedrons. According to Mitscherlich (Ann. Ch. Phys. [2] xxxiii. 394) the trioxide is also deposited in regular octahedrons from a solution in boiling soda. In each of its forms, it is isomorphous with one of the forms of trioxide of arsenic (arsenious oxide): the two bodies are therefore isodimorphous. Antimonious oxide is white or greyish-white at ordinary temperatures, but turns yellow when heated. It melts below a red heat, and sublimes when raised to a higher temperature in a close vessel. When heated in the air, it is partly converted into antimonic oxide. It is not decomposed by heat alone, but is reduced to the metallic state when heated with hydrogen, charcoal, or potassium.

Trioxide of antimony dissolves sparingly in *water*, more freely in strong *hydrochloric acid;* the latter solution is quite clear, provided the oxide is free from antimonic acid, but is rendered turbid by dilution with water. It dissolves when boiled with *aqueous tartaric acid*, and very easily in a solution of *acid tartrate of potassium* (cream of tartar), forming the *tartrate of antimony and potassium*, or *tartar-emetic*, $C^4H^4KSbO^7$. (See TARTRATES.)

It is quite insoluble in *nitric acid* of ordinary strength; but dissolves in cold fuming nitric acid, forming a solution which deposits pearly scales of a nitrate, $N^2O^5.2Sb^2O^3$ (Peligot). It dissolves also in *fuming sulphuric acid*, the solution depositing shining scales of a sulphate containing $3SO^3.Sb^2O^3$. It does not absorb *carbonic acid;* indeed, no carbonate of antimony is known to exist.

Trioxide of antimony acts as a feeble acid, forming salts called **antimonites**. The precipitated trioxide dissolves easily in *alkalis*, but the resulting compounds are very unstable, being decomposed by mere evaporation. The solutions give with nitrate of silver and excess of ammonia, a black precipitate insoluble in free ammonia. They reduce trichloride of gold, precipitating the metal. More stable salts, the antimonoso-antimonates, are formed by the union of the antimonites with antimonates (*vid. inf.*). The trioxide fused with caustic alkalis or their carbonates is converted into antimonic acid, which unites with the alkali. (Fremy.)

Tetroxide of Antimony, or Antimonoso-antimonic oxide, sometimes called *Antimonious acid*, Sb^2O^4.—This oxide is found native, as *Cervantite* or *Antimony-ochre*, forming acicular crystallisations, or massive, or as a crust or powder. It is yellow, or nearly white, of a greasy, bright or earthy lustre, and specific gravity 4·084. It is found at Pereta, in Tuscany (Dana, iii. 141). The same oxide is produced by the action of heat upon antimonic oxide (Sb^2O^5), by roasting the trioxide or trisulphide, or by treating pulverised antimony with excess of nitric acid. As thus prepared, it is white, infusible, and unalterable by heat; slightly soluble in water, more soluble in hydrochloric acid. It is easily resolved into antimonious and antimonic oxides. On boiling it with acid tartrate of potassium (cream of tartar) antimonious oxide dissolves, and antimonic oxide is left behind; and when a solution of the tetroxide in hydrochloric acid is gradually dropped into a large quantity of water, a precipitate of antimonious oxide is first produced, while antimonic acid remains in solution. From these and similar reactions, it has been inferred that the tetroxide is a compound of the trioxide and pentoxide, or an antimonate of antimony ($Sb^2O^3 + Sb^2O^5 = 2Sb^2O^4$). On the other hand, it is sometimes regarded as a distinct oxide, because it dissolves in alkalis, forming salts (often called *antimonites*), which may be obtained in the solid state. By fusing the tetroxide with hydrate or carbonate of potassium, exhausting with cold water, treating the residue with boiling water, and evaporating to dryness, a yellow, uncrystalline, saline mass is obtained, composed of $K^2O.Sb^2O^4$, and by mixing the solution of this salt with a small quantity of hydrochloric acid, a more acid salt, $K^2O.2Sb^2O^4$ is precipitated. By treating the same solution with a large quantity of acid, a precipitate is formed, consisting of the hydrated tetroxide, $H^2O.Sb^2O^4$. It is, however, more in accordance with the reactions above-mentioned, to regard these salts as antimonoso-antimonates, that is to say, as compounds of *antimonates* (containing Sb^2O^5) with antimonites (containing Sb^2O^3); thus the salt, $K^2O.Sb^2O^4$, may be regarded as $(K^2O.Sb^2O^3) + (K^2O.Sb^2O^5)$, or $KSbO^2.KSbO^3$.

The antimonoso-antimonates of the earth-metals and heavy metals are insoluble in water, and may be obtained by precipitation. Two of them are known as natural minerals, viz. — 1. *Romeine*, or (so-called) *Antimonite of calcium*, found at St. Marcel, in Piedmont, in groups of minute square-based octahedrons, of hyacinth-red, or honey-yellow colour; specific gravity 4·714 (in powder 4·675), hard enough to scratch glass. It contains 62·18 per cent. antimony, 15·82 oxygen, 16·29 lime, 1·31 iron, 1·21 protoxide of manganese, and 2·86 silica. The formula, $3Ca^2O.2Sb^2O^4$, requires 61·9 per cent., Sb, 22·7 O, and 15·4 Ca (Dana, ii. 410).—2. *Ammiolite*, or (so-called) *Antimonite of mercury*, occurs, mixed with clay and hydrated sesquioxide of iron, in the quicksilver mines in Chili, and at Silberg, near Olpe in Westphalia. It is a red powder, containing, according to Domeyko (Ann. Min. [4] vi. 183), 12·5 per cent. Sb^2O^4, 14·0 Hg^2O, 22·3 Fe^4O^6, 26·5 SiO^2, and 24·7 water (and loss). Probably only a mixture. (Dana, ii. 142.)

Pentoxide of Antimony, Antimonic Oxide or Anhydride, Sb^2O^5. In the hydrated state: **Antimonic Acid.**—This compound is obtained as a hydrate: —1. By treating antimony with nitric acid, or with aqua regia containing excess of nitric acid.—2. By precipitating a solution of antimonate of potassium with an acid. —3. By decomposing pentachloride of antimony with water.

The hydrated oxide obtained by either of these methods gives off its water at a heat below redness, and yields the pentoxide or anhydrous antimonic acid, as a yellowish powder. The same body is obtained by heating pulverised antimony with mercuric oxide till the green antimonate of mercury at first produced is decomposed and all the mercury driven off. It is tasteless, insoluble in water and in acids, and has a specific gravity of 6·6 (Boullay). At a red heat, it gives off oxygen, and is converted into the tetroxide. It is dissolved by boiling potash-ley, and when fused with carbonate of potassium expels carbonic anhydride and forms a salt, from which acids separate hydrated antimonic acid.

The hydrated oxides or acids obtained by the three methods above given, are by no means identical. That obtained by the first and second method is monobasic, and according to Berzelius, contains $Sb^2O^5.H^2O$ or $SbHO^3$; according to Fremy, $Sb^2O^5.5H^2O$, or SbH^3O^4, when air-dried at mean temperature; but the acid obtained by the action of water on pentachloride of phosphorus is dibasic, and contains, according to Fremy, $Sb^2O^5.4H^2O$. The monobasic acid is called *Antimonic acid;* the dibasic acid, *Metantimonic acid.* These acids are further distinguished by the following characters. Antimonic acid is a soft white powder, sparingly soluble in water, reddens litmus, and is dissolved, even in the cold, by strong hydrochloric acid and by potash-ley. The hydrochloric solution mixed with a small quantity of water, yields after a while, a precipitate of antimonic acid, but if diluted with a large quantity of water, it remains clear. Ammonia does not dissolve it in the cold. It is converted into metantimonic acid by heating with a large excess of hydrate of potassium.—Metantimonic acid dissolves in acids more readily than antimonic acid, and is dissolved by ammonia, after a while, even at ordinary temperatures. It likewise dissolves completely in a large quantity of water, and is precipitated therefrom by acids. It is very unstable, and easily changes into antimonic acid, even in water.

ANTIMONATES and METANTIMONATES.—Antimonic acid forms neutral or normal salts, containing $M^2O.Sb^2O^5$ or $MSbO^3$, and acid salts containing $M^2O.2Sb^2O^5$, or $Sb^2O^5.2MSbO^3$. Metantimonic acid, which is dibasic, forms normal salts containing $2M^2O.Sb^2O^5$, or $M^4Sb^2O^7$, and acid salts containing $2M^2O.2Sb^2O^5$, or $M^2O.Sb^2O^5$, so that the acid metantimonates are isomeric or polymeric with the neutral antimonates.* An acid metantimonate easily changes into a neutral antimonate (Fremy, Ann. Ch. Phys. [3] xii. 316, 357; xxii. 404).—Heffter (Pogg. Ann. lxxxvi. 411) analysed a series of antimonates, which, calculating from the old atomic weight of antimony (119), he supposed to contain 12 at. Sb^2O^5 to 13 at. of a base M^2O; but on recalculating the analyses with the new atomic weight (Sb = 120·3), it is found that they agree with the general formula $M^2O.Sb^2O^5$.

The metantimonates of ammonium, potassium, and sodium, are crystalline; the antimonates of the same bases are gelatinous and uncrystallisable. The soluble acid metantimonates form a crystalline precipitate with sodium-salts; the soluble antimonates do not form any such precipitate.

The antimonates and metantimonates of the alkali-metals are the only ones that are easily soluble in water. All the rest are insoluble or sparingly soluble, and may be obtained by precipitation.

Antimonate of Aluminium.—On adding the solution of an aluminium-salt to excess of antimonate of potassium, the whole of the alumina is precipitated in combination with antimonic acid, in white flocks, somewhat soluble in excess of the aluminium-salt.

Antimonate of Ammonium, $(NH^4)^2O.Sb^2O^5 + 2H^2O$, or $(NH^4)SbO^3 + H^2O$, separates as a white powder from a solution of antimonic or metantimonic acid in warm aqueous ammonia.—Neutral *metantimonate of ammonium*, $2(NH^4)^2O.Sb^2O^5$, is obtained in solution by treating metantimonic acid with *cold* aqueous ammonia; it is not easily obtained in the solid state. The solution mixed with a drop or two of alcohol, deposits a crystalline salt, which is the *acid metantimonate of ammonium*, $(NH^4)^2O.Sb^2O^5 + 6H^2O$. This salt is soluble in water, and the solution precipitates sodium-salts. It is very unstable, being converted, with loss of water, slowly at ordinary temperatures, and immediately at the boiling heat, into the insoluble neutral antimonate, with which it is isomeric.

Antimonate of Antimony, $Sb^2O^3.Sb^2O^5$.—The tetroxide of antimony is sometimes regarded as constituted in this manner (p. 317).

Antimonate of Barium, $Ba^2O.Sb^2O^5$, or $BaSbO^3$, is obtained by double decomposition, as a flocculent precipitate which gradually becomes crystalline; it dissolves slowly in aqueous chloride of barium.

Antimonate of Calcium, $Ca^2O.Sb^2O^5$, is a crystalline precipitate, which adheres closely to the sides of the vessel, like carbonate of calcium.

Antimonate of Cobalt, $Co^2O.Sb^2O^5$.—Reddish crystalline precipitate, which, when heated, gives off water, turns violet, and then black; when heated to redness, it becomes incandescent, and on cooling appears nearly white.—By mixing a solution of sulphate of cobalt with a hot solution of antimonate of sodium, Heffter (*loc. cit.*) obtained a flocculent rose-coloured precipitate, containing $Co^2O.Sb^2O^5 + 7H^2O$, and the mother-liquor, after standing for some days, deposited six-sided prisms containing $Co^2O.Sb^2O^5 + 12H^2O$.

Antimonate of Copper, $Cu^2O.Sb^2O^5$, or $CuSbO^3$, is a greenish crystalline powder, which when heated gives off 19½ per cent. water, and turns black. At a red heat, it glows like the cobalt-salt, turns white, and is afterwards unattackable by acids or alkalis in solution. On charcoal before the blowpipe, it is reduced to antimonide of copper.

Antimonates of Iron.—The *ferrous* salt is a white powder which becomes yellowish grey when dry, red by ignition, and is sparingly soluble in water. The *ferric* salt is light yellow.

Antimonate of Lead, $Pb^2O.Sb^2O^5$, or $PbSbO^3$, is obtained as a yellow anhydrous powder by fusing pentoxide of antimony with oxide of lead, or as a white hydrate by precipitation; the hydrate gives off its water when heated, and turns yellow.

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* If $O = 8$, the formulæ of the neutral and acid antimonates are $MO.SbO^5$ and $MO.2SbO^5$, and of the metantimonates, $2MO.SbO^5$ and $2MO.2SbO^5$ respectively.

A basic antimonate of lead, known by the name of *Naples Yellow*, is much used in oil-painting. It is obtained of the finest colour by mixing 2 pts. of chemically pure nitrate of lead with 1 pt. of the purest tartar-emetic and 4 pts. of common salt purified by repeated crystallisation, exposing the mixture for two hours to a heat just sufficient to fuse the chloride of sodium, and dissolving out the chloride of sodium with water; if the temperature has not been allowed to rise too high, the Naples yellow is then obtained in the form of a fine powder. — The same pigment is likewise obtained, but generally of a less brilliant colour, by fusing equal parts of antimony and lead with 3 pts. of nitre and 6 pts. of common salt.

Another basic antimonate of lead, $3Pb^2O.Sb^2O^5 + 4H^2O$, occurs native at Nertschinsk in Siberia, forming the mineral *Bleinierite*. It is amorphous, reniform, spheroïdal; also earthy or incrusting; sometimes with curved lamellar structure, specific gravity 3·933 (Karsten); 4·6—4·76 (Hermann). Lustre resinous, dull, or earthy. Colour grey, brownish, or yellowish. Opaque. Streak, greyish or yellowish. It is perhaps a mechanical mixture of lead and antimony ochres, and appears to result from the decomposition of other ores of antimony. (Hermann, J. pr. Chem. xxxiv. 179.)

Antimonate of Lithium. — Obtained by mixing a concentrated solution of chloride of lithium with antimonate of potassium, in flocks which soon become crystalline. It dissolves easily in hot water, and separates in grains on cooling. In dilute solutions, no precipitate is obtained.

Antimonate of Magnesium, $Mg^2O.Sb^2O^5 + 12H^2O$. — Separates by double decomposition from boiling solutions, in colourless shining hard crystals, which are isomorphous with the corresponding cobalt-salt, give off 8 per cent. water at 100° C., 10 per cent. at 200°, and 11 per cent. at 300°. (Heffter.)

Antimonate of Manganese. — White, altered by exposure to the air, sparingly soluble in water, somewhat more soluble in excess of the manganous salt. At a red heat, it becomes unattackable by acids, but does not glow.

Mercuric Antimonate, $Hg^2O.Sb^2O^5$, or $HgSbO^3$, is obtained by double decomposition as an orange-yellow precipitate. There is also an olive-green mercuric antimonate obtained by heating to low redness a mixture of 1 pt. powdered antimony, and 6 or 8 pts. mercuric oxide. At a stronger heat, this salt gives off oxygen and mercury, and leaves antimonic oxide. It is but little attacked by acids; but boiling hydrochloric acid dissolves a small quantity of it, and ammonia added to the solution throws down a light green powder.

Antimonate of Nickel. — Sulphate of nickel mixed with a boiling solution of antimonate of potassium, immediately forms a light green flocculent precipitate containing $Ni^2O.Sb^2O^5 + 6H^2O$, and the mother-liquor, after a few days, yields crystals of darker colours isomorphous with the magnesium-salt and analogous to it in constitution.

Antimonates of Potassium. — The neutral salt, $K^2O.Sb^2O^5 + 5H^2O$, is obtained by fusing 1 pt. of antimony with 4 pts. of nitre, digesting the fused mass in tepid water to remove nitrate and nitrite of potassium, and boiling the residue for an hour or two with water. The white insoluble mass of anhydrous antimonate is thereby transformed into a hydrate containing 5 at. water, which is soluble. The solution, when evaporated, leaves this hydrate in the form of a gummy uncrystallisable mass, which gives off 2 at. of water at 160° C., and the whole at a higher temperature. According to Heffter the anhydrous neutral antimonate is partly decomposed by prolonged boiling with water, an acid salt $2K^2O.Sb^2O^5$ remaining undissolved, and the liquid filtered therefrom yielding by evaporation the neutral salt with 7 at. water: $K^2O.Sb^2O^5 + 7H^2O$.

Acid Antimonate of Potassium is obtained by passing carbonic acid gas through a solution of the neutral antimonate. It is white, crystalline, perfectly insoluble in water, and is converted into the neutral salt when heated with excess of potash. This salt is the *antimonium diaphoreticum lavatum* of the pharmacopœias. (Fremy.) According to Heffter, the salt thus obtained is $2K^2O.3Sb^2O^5 + 10H^2O$.

Neutral Metantimonate of Potassium is prepared by fusing antimonic oxide or neutral antimonate of potassium with a large excess of potash. The fused mass dissolves in a small quantity of water, and the solution evaporated in vacuo yields crystals of the neutral metantimonate. This salt dissolves freely and without decomposition in warm water containing excess of potash; but cold water or alcohol decomposes it into potash and the acid matantimonate. Hence the aqueous solution of this salt gives a precipitate, after a while, with salts of soda. (Fremy.)

Acid Metantimonate of Potassium, $K^2O.Sb^2O^5 + 7H^2O$, sometimes called *granular antimonate of potassium*. — This salt is used as a test for soda. To obtain it, the neutral antimonate is first prepared and dissolved in the manner above described; the solution is filtered to separate any acid antimonate that may remain undissolved, then evaporated to a syrup in a silver vessel; and hydrate of potassium is added in lumps to convert the antimonate into metantimonate. The evaporation is then continued till the liquid begins to crystallise, which is ascertained by taking out a drop now and then upon a glass rod, and the liquid is then left to cool. A crystalline mass is thus obtained, consisting of neutral and acid metantimonate of potassium; the alkaline liquor is then decanted, and the salt dried upon filtering paper or unglazed porcelain (Fremy). This salt may also be prepared by treating trichloride of antimony with an excess of potash sufficient to redissolve the precipitate first formed, and adding permanganate of potassium till the solution acquires a faint rose colour. The liquid, filtered and evaporated, yields crystals of the granular metantimonate (Reynoso). This salt is sparingly soluble in cold water, but dissolves readily in water, between 45° and 50° C. When boiled with water for a few minutes, or kept in contact with water for some time, it is converted into the neutral antimonate. It must therefore be preserved in the solid state, and dissolved just before it is required for use. A small quantity of it is then treated with about twice its weight of cold water, to remove excess of potash, and convert any neutral metantimonate into the acid salt; the liquid is decanted; and the remaining salt is rapidly washed three or four times with cold water, then left in contact with water for a few minutes, and the liquid is filtered. On adding to the solution thus obtained a small quantity of any sodium-salt, a crystalline precipitate is formed, consisting of *acid metantimonate of sodium* (*vid. inf.*).

Antimonate of Sodium is obtained in tabular aggregates of small crystals, when the wash-water, resulting from washing a deflagrated mixture of antimony and nitre, is mixed with a sodium-salt. This salt has, according to Fremy, the composition $Na^2O.Sb^2O^5 + 7H^2O$. A salt of the same constitution is obtained, according to Heffter, in regular octahedrons, by boiling golden sulphide of antimony with caustic soda, and filtering the aqueous extract. It is nearly insoluble in cold water, soluble in about 350 pts. of boiling water. It gives off 2 at. water at 200° C., 2 at. more at 300°, and the rest at a red heat.

Acid Metantimonate of Sodium, $Na^2O.Sb^2O^5 + 7H^2O$, or $2NaHO.Sb^2O^5 + 6H^2O$.—This salt is produced when a solution of acid metantimonate of potassium, free from excess of alkali, is added to the solution of a sodium-salt. If the solution is not very dilute the precipitate is flocculent at first, but soon becomes crystalline. It is produced immediately in solutions containing not less than 1 pt. of sodium-salt in 300 pts. of liquid. In more dilute solutions, the precipitation is gradual, the metantimonate of sodium being deposited in crystals on the sides of this vessel, the effect being apparent after twelve hours, even in solutions containing not more that $\frac{1}{1000}$ pt. of sodium-salt. The precipitation is accelerated and rendered more complete by adding a little alcohol. The presence of free alkali retards it. The solution of sodium to be tested in this manner should be free from salts of lithium, ammonium, and the earth-metals, all of which, when diluted to a certain extent, yield precipitates of similar character. Acid metantimonate of sodium gives off 6 at. of water at 100°C., the seventh at about 300°.

Antimonate of Strontium.—Amorphous precipitate containing $Sr^2O.Sb^2O^5 + 6H^2O$.

Antimonate of Zinc, $Zn''O.Sb^2O^5$.—Crystalline precipitate somewhat soluble in excess of the zinc-salt. When heated, it gives off water and turns yellow, but without incandescence. On charcoal before the blowpipe it does not fuse; neither is it reduced without addition of alkali.

ANTIMONY, OXYCHLORIDE OF. *Basic Chloride of Antimony, Powder of Algaroth, Pulvis Algarothi s. angelicus, Mercurius Vitæ*, &c.—A compound formed by the action of water on trichloride of antimony. It was formerly much used in medical practice, but now serves chiefly for the preparation of pure antimonious oxide and tartar-emetic. The best way of preparing it is to boil commercial sulphide of antimony in fine powder with strong hydrochloric acid, till the liquid is saturated, sulphuretted hydrogen escaping all the while; leave the solution to cool; add to it, with agitation, small portions of water till it begins to show turbidity; then filter; mix the filtrate with five to ten times its bulk of water; and wash the resulting precipitate thoroughly with cold water by decantation or on the filter. The addition of a small quantity of water and filtration before the complete precipitation, is necessary, in order to remove a small quantity of hydrosulphuric acid, which always remains in the acid liquid, but is carried down by the first portions of oxychloride precipitated, and thereby removed: if allowed to remain, it would cause the precipitate to turn yellow.

The dried precipitate is a heavy white amorphous powder; but if left to stand in the liquid, or if boiled with it, is converted into a mass of small shining oblique rectangular prisms. It varies in composition according to the temperature of the water used for the precipitation and washing. According to Duflos and Bucholz, it is

$2SbCl^3.5Sb^2O^3$; according to Johnston, $4SbCl^3.9Sb^2O^3$; according to Schneider, $2SbOCl.Sb^2O^3$; according to Peligot, the precipitate formed in the cold is $SbCl^3.Sb^2O^3$, or SbO.Cl, (chloride of antimonyl), and after it has become crystalline by heating, $2SbCl^3.5Sb^2O^3$. Continued washing with water removes more and more of the chloride, ultimately leaving nearly pure antimonious oxide; alkaline-water removes the whole of the chloride. The oxychloride is also decomposed by heat, the chloride being volatilised and oxide remaining.

Antimonious oxide dissolves in about 15 times its weight of the boiling trichloride, and the solution on cooling solidifies into a pearly grey, perfectly crystalline mass, apparently consisting of $Sb^2OCl^4.6SbCl^3$, analogous to the sulphochloride formed in like manner (p. 338). It is decomposed by absolute alcohol, with separation of powder of algaroth. (Schneider, Pogg. Ann. cviii. 407.)

ANTIMONY, OXYIODIDE OF. Antimonious iodide is decomposed by water, yielding a white precipitate, which appears to be analogous in composition to the oxychloride. An oxyiodide, $2SbI^3.5Sb^2O^3$, is likewise obtained in gold-coloured spangles resembling iodide of lead, by adding iodine to a solution of tartar-emetic, or by treating the trichloride of antimony with solution of iodide of potassium, evaporating the solution, treating the residue with water, and repeating these operations several times. It is decomposed by heat. Hydrochloric acid dissolves it, with separation of iodine. It is slightly soluble in tartaric acid and cream of tartar. Nitric acid decomposes it, separating oxide of antimony. (Preuss, Pharm. Centr. 1839, p. 311.)

ANTIMONY, OXYSULPHIDE OF. The compound $Sb^2O^3.2Sb^2S^3$ occurs native as *Red antimony, Antimony blende, Kermesome, Rothspiessglanzerz*, in needles or tufts of capillary crystals belonging to the monoclinic system: Specific gravity = 4·5 to 4·6. Hardness = 1 to 1·5. It has a cherry-red colour and adamantine lustre, gives a brownish-red streak, and is slightly translucent, appearing scarlet by transmitted light. Melts very readily before the blowpipe, sinking into the pores of the charcoal, and volatilising in dense clouds. Ignited in a current of hydrogen, it yields hydrosulphuric acid, water, and metallic antimony (H. Rose, Pogg. Ann. iii. 452). It contains 74·5 to 74·7 Sb, 5·29 to 4·7 O, and 20·5 S. Occurs in veins in quartz, accompanying grey and white antimony, at Malaczka near Posing in Hungary, at Bräunsdorf near Freiberg, and at Allemont in Dauphiny. It appears to result from alteration of grey antimony ore. A similar compound, but of an orange-red colour and containing only 17·9 per cent. sulphur, sublimes when aqueous vapour is passed over the ignited trisulphide. (Regnault.)

Various oxysulphides of antimony may be prepared artificially. They were formerly much used in pharmacy for the preparation of tartar-emetic, but are now nearly obsolete. α. *Antimonial crocus* or *saffron* (*Crocus antimonii, s. metallorum*) is a brownish-yellow substance, prepared by fusing a mixture of 3 pts. of the trioxide and 1 pt. trisulphide of antimony, or an oxide of antimony with the proper proportion of sulphur. A similar compound, mixed however with variable quantities of antimonite of potassium, is obtained by treating the trisulphide with caustic alkalis (p. 332). β. *Glass of antimony* (*Vitrum antimonii*) is an oxysulphide prepared by roasting the grey sulphide at a moderate heat, till it is converted into the tetroxide, and fusing this *antimony ash* in an earthen crucible, with about $\frac{1}{20}$ of its weight of sulphur. It is a brilliant substance, varying in colour from yellowish-red to hyacinth-red, according to the proportions used. It gives up its oxide to acids, and evolves sulphuretted hydrogen when treated with hot hydrochloric acid. γ. A compound of trisulphide of antimony with a very small portion of oxide, called *Regulus antimonii medicinalis* or *Rubinus antimonii*, is obtained by fusing 5 pts. of the grey sulphide with 1 pt. of pearl-ash, and separating the upper stratum (consisting of sulphantimonite of potassium) from the lower. It is a black mass, having a brilliant conchoïdal fracture, and yielding a dark grey powder.

According to Liebig, mineral kermes prepared by the action of alkaline carbonates on the amorphous trisulphide, is a definite oxysulphide of antimony (see p. 328); but kermes obtained by most other modes of preparation, appears to contain the oxide merely in a state of mixture with the sulphide.

ANTIMONY, SELENIDE OF. Antimony and selenium unite when heated together, to a lead-grey crystalline mass, the combination being attended with rise of temperature, often amounting to ignition. The same compound is formed by precipitating a solution of tartar-emetic with seleniuretted hydrogen; hence its formula is probably Sb^2Se^3. Selenide of antimony is easily fusible, and oxidises when heated in the air, giving off selenious acid. Heated with trioxide of antimony, out of contact with the air, it melts into a mass resembling the fused sulphide.

ANTIMONY, SULPHIDES OF. Antimony forms two sulphides, Sb^2S^3 and Sb^2S^5, corresponding to antimonious and to antimonic oxide, and perhaps also an intermediate sulphide corresponding to the tetroxide.

TRISULPHIDE OF ANTIMONY, ANTIMONIOUS SULPHIDE, ANHYDROUS SULPHANTIMONIOUS ACID, Sb^2S^3, or SbS^3.—This compound exists in the crystalline and in the amorphous state.

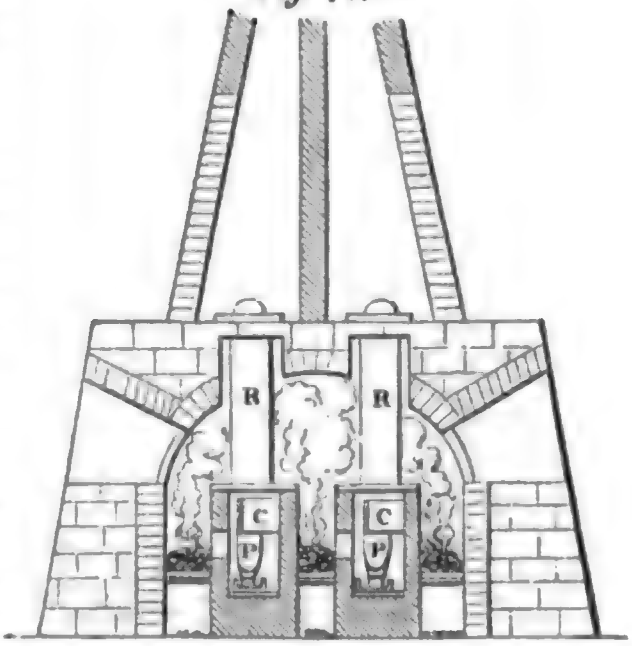
1. The *crystallised* trisulphide occurs as a natural mineral called stibnite, stibine, grey antimony, antimony-glance (*Spiessglanz*, *Grauspiessglanzerz*, *Antimoine sulfuré*, *Leo ruber*, *Plumbum nigrum*, *Lupus metallorum*). It is the source of all the antimony of commerce. It is found in various localities in Hungary, Germany, and France, also in Cornwall, in Dumfriesshire, in Maine, Maryland, and New Hampshire (U. S.), and abundantly in Borneo,—always associated with the older rocks, such as gneiss, quartz, clay-slate, mica-slate, limestone, porphyry, &c., whence it is separated by simple fusion, yielding the *crude antimony* of commerce.

The separation of the sulphide from the accompanying gangue is effected in various ways. The simplest arrangement is that which is in use at Malbosc in the department of Ardèche, in France, and at Wolfsberg in the Harz. A number of conical pots, perforated at bottom, and standing upon receivers sunk in the ground, are placed twenty-five or thirty in a row, between walls about nine inches high, the space between the pots being filled with coal, and the fire lighted with brushwood. Each pot holds about 45 kilogrammes of ore, and in forty hours four meltings are made, sufficient to fill the receivers. The advantages of this method are that it saves the expense of erecting a furnace, and may be carried on at any place to which the ore and fuel can be most easily transported. But it involves a large consumption of fuel, and is therefore advantageous only where fuel is very abundant. At Malbosc the consumption is 300 kilogrammes of coal and 40 kil. of wood, for every 100 kil. of crude antimony produced.

Another method, somewhat different from the above, consists in heating the conical pots by the flame of a reverberatory furnace, the receivers being placed below the hearth. This arrangement is also in use at Wolfsberg, and at La Lincouln in Haute Loire. At Schmöllnitz in Hungary, the pots are likewise heated by a reverberatory furnace; but the melted sulphide runs through a channel into receivers placed outside the furnace. This arrangement effects a considerable saving of time and fuel, as it enables the pots to be filled and emptied without putting out the fire.

In some localities, cylindrical tubes are used in preference to conical pots, as being more durable. An arrangement of this kind is in use at Malbosc. The ore is placed in large cylinders R R (*fig.* 71) each holding 500 pounds of ore, and four being heated in each furnace. The cylinders are perforated at bottom, and stand on plates pierced with corresponding apertures. Beneath these plates, in the chambers C C, are placed earthen pots P P, to receive the melted sulphide. The process lasts three hours, and when it is finished, the residues are taken out, either through the top of the furnace, or through apertures in the lower part of the cylinders (which are stopped with clay during the melting), and then the cylinders are refilled. With this arrangement, 64 pts. of coal are consumed for every 100 pts. of crude antimony produced.

Fig. 71.



Lastly, the ore is sometimes heated on the hearth of a reverberatory furnace, without the use of either pots or cylinders. The furnace has an inclined hearth, and the fused sulphide flows into a receiver placed outside. This arrangement, which is in use at Linz, in Prussia, and at Ramé in La Vendée, effects a great saving of fuel, and likewise does away with the expense of the containing vessels; but it involves a considerable loss of sulphide of antimony by volatilisation, and is therefore adopted only where fuel is very dear.

Whatever arrangement may be adopted, it is important that the ore be not broken into very small pieces. If it be too much divided or pulverised, the melted sulphide cakes together with the gangue, and is very difficult to separate. Too great heat must also be avoided, as at a white heat, sulphide of antimony is perfectly volatile. The residues always contain 10 or 12 per cent. of antimony, partly as sulphide, partly as oxide. [For further details, see Bruno Kerl's "Handbuch der metallurgischen Hüttenkunde," Freiberg, 1858, iii. 25.]

Native sulphide of antimony crystallises in prisms belonging to the trimetric system, with four-sided summits resting on the lateral faces. Cleavage very distinct, parallel to the shorter diagonal and the principal axis. Specific gravity 4·516 (Haüy); 4·62 (Mohr). Hardness = 2. It is sectile, and in thin laminæ slightly flexible; fracture subconchoïdal. It has a metallic lustre and lead-grey colour, inclining to steel-grey, sometimes iridescent. Produces a streak of the same colour. The fused sulphide generally forms blackish-grey, radiating, specular masses, having a steel-grey lustre. It is easily fusible, thin splinters melting even in the flame of a candle.

The native sulphide is seldom pure, being generally contaminated with lead, copper, iron and arsenic. Wittstein found in four samples of *crude antimony:*

	a	*b*.	*c*.	*d*.
Antimony	62·48	59·67	70·26	71·98
Lead	10·40	11·96		
Iron	0·70	0·63	0·31	
Arsenic	trace	trace		
Sulphur	26·42	27·74	29·43	28·02
	100·00	100·00	100·00	100·00

a. Iridescent, from Kronach in Upper Franconia; *b*. Non-iridescent, from the same locality; *c*. Hungarian; *d*. English.

The best way of detecting these impurities is to heat the finely pulverised mineral with strong hydrochloric acid, till it is completely decomposed. Lead, if present in any considerable quantity, will then separate on cooling, as crystallised chloride; water added to the solution will throw down oxychloride of antimony, while iron, copper, arsenic, and a little lead will remain in solution; copper may then be detected by ammonia, iron by ferrocyanide of potassium, lead by sulphuric acid.

To detect arsenic, the pulverised mineral is deflagrated with nitrate and carbonate of sodium; the fused mass boiled with water, the filtrate acidulated with hydrochloric acid, and sulphurous acid added to reduce the arsenic acid to arsenious acid, which may then be precipitated by sulphuretted hydrogen. The precipitate, however, may likewise contain sulphide of antimony, and must therefore be further examined.

To obtain *pure* crystallised trisulphide of antimony, it is best to prepare it artificially, by fusing pure metallic antimony with sulphur. 13 pts. of finely pulverised antimony are mixed as intimately as possible with 5 pts. of flowers of sulphur, and the mixture is thrown by small portions into a heated crucible, care being taken not to add a fresh portion till the combination of the last portion is completed, which may be known by the incandescence which accompanies the action. When the whole has been added, the crucible is covered and left to cool. If any portion of the antimony remains uncombined, it will sink to the bottom of the fused mass, and may easily be separated from the sulphide after cooling. It is sometimes recommended to remelt the product two or three times with smaller quantities of sulphur.

The *reactions* of crystallised sulphide of antimony are the same as those of the amorphous sulphide, to be presently described: but they take place less quickly, on account of the greater cohesion of the mass.

Amorphous Trisulphide of Antimony, Mineral Kermes.—Brown-red sulphide of Antimony, Pulvis Carthusianorum, Sulphur stibiatum rubrum, Stibium sulphuratum rubrum.—This substance is prepared by a great variety of processes, some of which yield the pure trisulphide, differing from the native compound only in colour and in the absence of crystalline structure, while others yield the sulphide more or less mixed with the trioxide, and sometimes with other antimonial compounds.

a. The pure amorphous sulphide may be obtained by the following processes.—1. By keeping the grey trisulphide in the fused state for a considerable time, and then cooling it very suddenly by throwing the vessel in which it has been melted into a large quantity of cold water (Fuchs).—2. By dissolving the native sulphide in potash-ley, and precipitating by an acid (Liebig).—3. By igniting 1 pt. of *crude antimony* with 2 pts. of black flax (a mixture of 1 pt. nitre, and 2 pts. cream of tartar), boiling the ignited mass with water, and mixing the clear filtrate with an alkaline carbonate, whereby the pure amorphous sulphide is precipitated (Liebig).—4. By the decomposition of alkaline sulphantimonites (livers of antimony).—5. By treating mineral kermes containing oxide of antimony, with tartaric acid, whereby the oxide is dissolved out.

b. *Mineral Kermes containing oxide* is obtained by the action of alkalis on the trisulphide. The oldest method, given by La Ligérie, consists in boiling the finely pulverised grey sulphide with the solution of an alkaline carbonate, and leaving the filtered solution to cool: the same process is given in the last edition of the Prussian Pharmacopœia. As however, crystallised sulphide of antimony dissolves but slowly in alkaline carbonate, it is better first to convert the crystallised into the amorphous sulphide, and prepare the kermes from the latter. The following is the process given by Liebig (Handw. d. Chem. 2te Aufl. ii. 121).

1 pt. of the pulverised grey sulphide is boiled for an hour with 1 part of solid caustic potash and 30 pts of water (or 1 pt. of the grey sulphide with 4 pts. potash-ley of specific gravity 2·25 and 12 pts. water, or 1 pt. sulphide, with 1 pt. carbonate of potassium, 1½ pts. slaked lime, and 15 pts. water), and the filtered liquid is mixed with dilute sulphuric acid, whereby amorphous sulphide of antimony is precipitated. The thickish mixture is then divided into three parts, and covered with water in three separate vessels; the precipitate is left to settle; the water is decanted; and fresh water added till the precipitates are well washed: they are then placed upon three separate filters. 1 pt. of anhydrous (or 2·7 pts. of crystallised) carbonate of sodium is next dissolved in 34 pts. of water; the precipitate from the first of the three filters is introduced into the filtered solution; the liquid is boiled for an hour; and the solution, which has taken up all the sulphide of antimony, is left to cool, whereupon it deposits kermes. The supernatant liquid is now brought to the boiling heat, the second precipitate is added to it and treated in the same manner, and finally the same processes are repeated with the third. The finest coloured kermes is deposited from the second boiling. The precipitates are washed with cold water: their weight after drying, amounts to nearly the half of the grey sulphide used. [For the rationale of the process, see DECOMPOSITIONS OF SULPHIDE OF ANTIMONY, p. 333.]

The solution obtained by boiling the grey sulphide with caustic potash or soda deposits kermes on cooling, provided the alkali is not in great excess; and by boiling the mother-liquors remaining after the deposition of the kermes with the undissolved portion of the grey sulphide, fresh deposits, smaller in quantity, may be obtained. According to Duflos, the solution obtained by boiling 100 pts. of grey sulphide for a quarter of an hour with a solution of 30 parts of hydrate of potassium in 300 pts. of water, deposits on cooling 25 pts. of kermes; a second boiling of the mother-liquor with the undecomposed grey sulphide yields 10 pts.; a third yields 2·3 pts. The successive deposits thus formed are continually richer in oxide of antimony.

A solution containing so much alkali as not to yield any deposit on cooling, yields a precipitate of kermes when carbonic acid gas is passed through it, and afterwards an additional quantity when treated with strong acids. The precipitate thus formed generally contains a little oxide, and always a sulphantimonate of potassium or sodium, of the form $K^2S.Sb^2S^5$, because, according to H. Rose, part of the antimony is oxidised by the air, and gives up its sulphur to the trisulphide of antimony, thereby converting it into pentasulphide.

Kermes may likewise be obtained by boiling sulphide of antimony with potash-ley and sulphur, or by boiling a solution of sulphantimonite of sodium with metallic antimony. There are also several other modes of preparation, for which we must refer to Gmelin's Handbook, vol. iv. pp. 340—349, where they are fully described. The preparations obtained by these different methods, are, however, by no means identical; they contain variable proportions of oxide of antimony, and many of them likewise contain sulphantimonite of potassium or sodium.

Properties.—The pure amorphous trisulphide obtained by Fuchs's method is a dense fissured mass, harder than the native sulphide, having a conchoïdal fracture, a grey colour, or in thin pieces, dark hyacinth-red, and yielding a red-brown powder somewhat lighter in colour than ordinary kermes; its specific gravity is 4·15. The pure amorphous sulphide prepared by other methods is a brown-red, loosely coherent powder, which makes a brown streak on paper. It is lighter than the native sulphide, and does not conduct electricity. It contains water, which it gives off below 100° C. When treated for some time with cold hydrochloric acid, or when fused and very slowly cooled, it is converted into the crystalline sulphide.

Ordinary kermes containing oxide is a brown-red loose powder, which becomes blackish-grey when washed with boiling water. By fusion and slow cooling, it is converted into a slag-like mass, totally destitute of crystalline structure, a property by which it differs essetnially from the pure amorphous sulphide.

Hydrated Trisulphide of Antimony.—The amorphous sulphide is obtained as a hydrate by passing sulphuretted hydrogen through an acid solution of the trichloride, or through a solution of tartar-emetic acidulated with acetic acid. The precipitate at first formed in a solution of the trichloride acidulated with tartaric acid, is a mixture of the hydrated sulphide with oxychloride; but on continuing the passage of the gas, it becomes darker in colour, and is completely converted into the hydrated sulphide. The precipitate obtained by decomposing a solution of sulphantimonate of potassium with sulphuric acid is probably also the hydrated sulphide.

Hydrated trisulphide of antimony when dry has a fine dark orange-colour. It gives off water when moderately heated, but to dehydrate it completely, requires a temperature of 200° C. it then turns black. At higher temperatures, it melts and solidifies in the crystalline form on cooling.

Decompositions of Trisulphide of Antimony.—The reactions of this compound are nearly the same, whether it be in the crystalline or in the amorphous state, the crystalline variety merely acting less quickly on account of its closer state of aggregation.—1. The dry amorphous sulphide touched with a red-hot body burns away in the *air* with a glimmering light, producing sulphurous anhydride, antimonious oxide, and antimonic oxide; the grey sulphide heated above its melting point, burns with a blue flame, yielding the same products.—2. The recently precipitated amorphous sulphide is decomposed by boiling for some time with a large quantity of *water*, yielding hydrosulphuric acid and antimonious oxide, which dissolve. Vapour of water passed over red-hot sulphide of antimony likewise yields hydrosulphuric acid and antimonious oxide, the latter combining with undecomposed sulphide, and an orange-yellow body subliming.

3. *Chlorine*, with the aid of heat, *decomposes* the trisulphide completely, forming trichloride of antimony and chloride of sulphur.—4. Heated in *hydrochloric acid gas* or boiled with the strong aqueous acid, it gives off hydrosulphuric acid, and forms trichloride of antimony, which in the latter case dissolves in the excess of acid.—5. With *strong sulphuric acid*, it yields sulphurous anhydride and antimonious sulphate, the sulphur being separated as a compact mass.—6. With *strong nitric acid*, it forms antimonious oxide and sulphuric acid, part of the sulphur, however, being set free and remaining mixed with the oxide.—7. *Aqua-regia* containing excess of hydrochloric acid dissolves the trisulphide, forming trichloride of antimony and sulphuric acid, and leaving a residue of sulphur often mixed with a little antimonic acid.—8. The trisulphide ignited with *nitrate of potassium or sodium*, is violently oxidised, being completely converted into sulphuric and antimonic acids, if 17 pts. or more of nitre are used to 10 of antimony; with less nitre, a compound of sulphide of potassium, sulphide of antimony and antimonic oxide is likewise formed.—9. Many metals, *e. g. iron*, *potassium*, and *sodium* (or a mixture of carbonate of potassium or sodium with charcoal), decompose sulphide of antimony at a red heat, the resulting metallic sulphide sometimes uniting with undecomposed sulphide of antimony; if, on the other hand, the reducing metal is in excess, it sometimes forms an alloy with the reduced antimony.

10. The *fixed caustic alkalis* decompose trisulphide of antimony in the same manner in the wet and in the dry way, forming trioxide of antimony and a sulphide of the alkali-metal:

$$Sb^2S^3 + 3K^2O = 3K^2S + Sb^2O^3,$$

but the final products of the action vary according to the state of aggregation of the antimonious sulphide, the temperature to which the mixture is exposed, and the proportions of the two substances present. *a.* When amorphous sulphide of antimony, prepared in the wet way, is triturated with cold potash-ley, it dissolves *completely* up to a certain point, the sulphide of potassium formed as above, taking up undecomposed sulphide of antimony, and the antimonious oxide dissolving in the potash. This solution contains sulphantimonite and antimonite of potassium. When treated with acids, it yields a precipitate of antimonious sulphide, without evolution of sulphuretted hydrogen, because the quantity of that compound evolved by the decomposition of the sulphide of potassium present, is but just sufficient to convert the trioxide of antimony into trisulphide. But if the addition of the trisulphide be continued, a point is at length reached, at which the alkaline liquid cannot take up any more antimonite of potassium, and any further quantity of antimonious oxide then formed remains undissolved, partly combined with potash, partly with antimonious sulphide, forming the mixture called *crocus antimonii* (328). The *incomplete* solution thus formed contains, however, a larger proportion of sulphide of potassium than the complete solution, the excess being proportional to the quantity of oxide left undissolved. This excess of sulphide of potassium takes up an additional quantity of sulphide of antimony, and the solution treated with acids, evolves sulphuretted hydrogen, besides giving a precipitate of antimonious sulphide. The *complete* solution mixed with carbonate of ammonium, or with acid carbonate of potassium or sodium, yields a dirty brown precipitate consisting of 3 at. antimonious sulphide with 1 at. sulphide of potassium or sodium, a portion of the alkaline sulphide also remaining in the liquid. The greater part of the alkaline antimonite is likewise precipitated, because the caustic alkali which held it in solution is converted into neutral carbonate. The precipitation of the antimonious oxide, is, however, partly caused by its affinity for the sulphide of antimony previously thrown down in combination with the alkali-metal. The *incomplete* solution is decomposed in like manner, but the precipitate contains a smaller proportion of antimonic oxide. The *complete* solution rapidly absorbs oxygen from the air; the sulphide of potassium is first decomposed, yielding oxide of potassium and sulphur, which then converts the trisulphide of antimony into pentasulphide:

$$3K^2S + Sb^2S^3 + O^2 = 2K^2O + K^2S.Sb^2S^5$$

so that the solution treated with acids yields a precipitate of pentasulphide of antimony; and subsequently the antimonite of potassium is converted into antimonate, which collects in crystals at the bottom.

b. When antimonious sulphide in excess is digested with *hot caustic alkalis*, the products formed are the same as in the cold, excepting that the sulphide of potassium then takes up a larger proportion of antimonious sulphide, the excess of which is subsequently deposited on cooling; not, however, in the pure state, but in combination, partly with alkaline sulphide, partly with antimonious oxide, the composition of the precipitate being, in fact, similar to that which is produced by alkaline bicarbonates in a cold-prepared solution of antimonious sulphide. The supernatant liquid gives with alkaline bicarbonates a precipitate of alkaline sulphantimonite free from oxide.

All the precipitates above-mentioned are altered in composition by prolonged treatment with cold water containing air, or with boiling water, antimonious oxide being dissolved out, in combination with alkali, and pure dark-coloured antimonious sulphide remaining.

c. Crystalline antimonious sulphide is acted upon by *caustic alkalis* in the same way as the amorphous sulphide, but less easily, and when the action takes place in the cold, a residue of *crocus antimonii* is always left, whatever may be the quantity of alkali present. The resulting solution exhibits the reactions of the *incomplete* solution above-mentioned.

11. *Alkaline carbonates*, fused with antimonious sulphide, either crystalline or amorphous, give off carbonic anhydride, and form antimonious oxide and a sulphide of the alkali-metal, the fused mass containing these products in combination with excess of antimonious sulphide and alkali. With 4 pts. antimonious sulphide and 1 pt. alkaline carbonate, an easily fusible mass is formed, which, after cooling, has an iron-grey colour, is perfectly homogeneous, and *is not attacked by water*. A mixture of 2 pts. carbonate to 1 pt. antimonious sulphide requires a strong red heat to melt it, and yields on cooling 12 per cent. of metallic antimony, together with a light brown liver of antimony, which deliquesces in the air, and is *perfectly soluble in water*. The separation of the metallic antimony results from decomposition of the alkaline antimonite contained in the mass, part of it being converted into antimonate. With intermediate proportions, the mixture fuses more readily, and the resulting liver of antimony is less soluble in water as the proportion of antimonious sulphide is greater. The insoluble residue contains the excess of antimonious sulphide in combination with a portion of the alkaline sulphide and with antimonious oxide; it is, in fact, similar in composition to the *crocus* prepared in the wet way, but generally contains more sulphide of antimony. Water acts upon these livers of antimony exactly in the same manner as solutions of the caustic alkalis act upon antimonious sulphide under the same circumstances.

Solutions of alkaline carbonates do not act on antimonious sulphide in the cold, but at the boiling heat, they dissolve the amorphous sulphide readily, the crystalline slowly. The hot solution, prepared out of contact with the air, contains the same products as the *complete* solution of the amorphous sulphide in cold potash-ley (p. 332). It becomes turbid on cooling, and deposits a grey-brown precipitate similar in composition to that which is produced by alkaline bicarbonates in the cold complete solution just mentioned, consisting, in fact, of two compounds, viz. an alkaline sulphantimonite and an oxysulphide of antimony. The liquid, after the separation of this precipitate, retains a certain portion of alkaline sulphide.

If the solution of antimonious sulphide in hot alkaline carbonate be boiled for some time in contact with the air, part of the alkaline sulphide becomes oxidised, and gives up part of its sulphur to the dissolved trisulphide of antimony, thereby converting it into pentasulphide, which remains in solution after cooling. The quantity of antimonious oxide in the precipitate remains the same, but the proportion of antimonious sulphide in it is diminished by the quantity thus retained in solution. The proportion of sulphide of sodium is likewise diminished by the oxidation. The quantity of antimonious oxide in the precipitate is now not only sufficient to replace all the alkaline sulphide in combination with the precipitated antimonious sulphide, but a certain quantity of alkaline antimonite likewise remains free in the liquid; and there is precipitated a *compound of trioxide and trisulphide of antimony*, which is the true **medicinal kermes**; it is generally, however, mixed with small quantities of alkaline antimonite.

Kermes prepared in this manner, contains, under all circumstances, a tolerably constant quantity of antimonious oxide, because, when alkaline carbonates are used, the portion of sulphide of antimony attacked by them passes *completely* into the solution, without leaving any residue, and consequently the entire quantity of the products thus formed is likewise contained in the liquid. (Liebig, Handwört. d. Chem. 2te. Aufl. ii. 125—130.)

12. By ignition with *baryta*, *strontia*, *lime*, and other *oxides*, antimonious sulphide is decomposed in the same manner as by caustic and carbonated alkalis: the products are insoluble in water, and consist of mixtures of metallic sulphantimonites with an oxysulphide of antimony.

Sulphantimonites.—Trisulphide of antimony is a sulphur-acid, uniting with basic metallic sulphides. Some of these compounds, containing the sulphides of the heavy metals, are natural minerals, viz.:

Zinkenite	$Pb^2S . Sb^2S^3$
Miargyrite	$Ag^2S . Sb^2S^3$
Antimonial Copper-glance	$Cu^4S . Sb^2S^3$
Plagionite	$4Pb^2S . 3Sb^2S^3$
Jamesonite	$3Pb^2S . 2Sb^2S^3$
Feather-ore	$2Pb^2S . Sb^2S^3$
Boulangerite.	$3Pb^2S . Sb^2S^3$
Pyrargyrite	$3Ag^2S . \left.\begin{matrix}Sb^2\\As^2\end{matrix}\right\}S^3$
Bournonite	$3(Cu^4S.Sb^2S^3) + 3Pb^2S.2Sb^2S^3)$
Fahl-ores	$2\begin{pmatrix}Zn^2S\\Fe^2S\end{pmatrix} + \begin{pmatrix}Sb^2S^3\\As^2S^3\end{pmatrix}$
Stephanite	$6Ag^2S . Sb^2S^3$
Polybasite	$9\begin{pmatrix}Ag^2S\\Cu^4S\end{pmatrix} + \begin{pmatrix}Sb^2S^3\\As^2S^3\end{pmatrix}$
Berthierite	$3Fe^2S . 2Sb^2S^3$
Variety of Berthierite, from Anglar . .	$Fe^2S . Sb^2S^3$
Variety of Berthierite, from Marturet . .	$3Fe^2S . 4Sb^2S^3$

In these formulæ, the elements whose symbols are written one above the other, replace one another isomorphously. [For description, see the names of the several minerals.]

The most important of the artifically prepared sulphantimonites are those which contain the protosulphides of the alkali-metals: they are called Livers of Antimony (*Hepar Antimonii*). They are obtained, mixed with oxide in various proportions, by fusing the trisulphide of antimony with alkaline carbonates, or metallic antimony with sulphate of potassium; and free from oxide, by melting sulphide of antimony with alkaline sulphates and charcoal, or with alkaline carbonates, sulphur and charcoal, or again by melting sulphantimonate of sodium with metallic antimony.

These alkaline sulphantimonites, or livers of antimony, are easily fusible, and deliquescent or unalterable in the air, according to the proportion of the alkaline sulphide and the antimonious sulphide contained in them. They are more or less soluble in water, when the ratio of the antimonious sulphide to the alkaline sulphide is less than 2 : 1; insoluble, when it is greater.

In the fused state, they are black or black-brown and crystalline. Their solutions boiled with pulverised antimonious sulphides, dissolve an additional quantity of it, which on cooling is deposited as a flocculent precipitate containing also the alkaline sulphide. Acids added to the solutions throw down the amorphous sulphide; so likewise does carbonate of ammonium. Alkaline bicarbonates immediately throw down sulphantimonite of potassium or sodium; the solution mixed with an alkaline monocarbonate, remains clear at first, but solidifies after a while to a tremulous jelly containing the same compound. The same effect is produced when the aqueous solution of a liver of antimony is diluted with a large quantity of cold water. The solution of a liver of antimony changes very quickly when exposed to the air, a sulphantimonate being formed in solution, and a portion of the trisulphide of antimony being separated in brown metallic films or as a powder.

Pentasulphide of Antimony; Antimonic Sulphide; Anhydrous Sulphantimonic Acid.—*Persulphide of Antimony; Golden Sulphuret of Antimony; Sulphur Antimonii auratum*, Sb^2S^5, or SbS^5.—This compound is not found native. It is prepared: 1. By passing sulphuretted hydrogen through a mixture of the pentachloride with water and tartaric acid, or through antimonic oxide suspended in water.—2. By decomposing the solution of the sulphantimonate of an alkali-metal with an acid, the sodium-salt, for example, whereby the sulphide of sodium is decomposed, a salt of the alkali metal being formed, with evolution of sulphuretted hydrogen, and pentasulphide is precipitated:

$$\underset{\text{Sulphantimonate of sodium.}}{3Na^2S.Sb^2S^5} + 6HCl = 6NaCl + 3H^2S + Sb^2S^5.$$

[For details see Gmelin's Handbook, iv. 355; Handwörterb. d. Chem. 2^{te} Aufl. ii. 133.]

Pentasulphide of antimony is a yellowish-red powder, or loosely agglomerated mass, without any trace of crystalline structure; it has a very feeble odour of sulphur, a sweetish sulphurous taste, and is slightly emetic. Heated in close vessels to the boiling point of sulphur, it is resolved into the trisulphide and free sulphur. It burns with flame when heated in the air. Exposed to the air in the moist state, it is partly converted, after a while, into the trioxide of antimony.—Hot *hydrochloric acid* decomposes it, giving off sulphuretted hydrogen, separating sulphur, and forming an aqueous solution of trichloride of antimony; cold hydrochloric acid imparts to it a greyish colour, perhaps in consequence of the formation of the trisulphide and liberation of 2 at. sulphur.—Triturated, out of contact of air, with aqueous *ammonia*, it dissolves completely, more easily in a warm acid than in a cold solution, and is precipitated therefrom by acids. If the pentasulphide contains trisulphide, the latter remains as a brown residue; a yellow or white residue, on the other hand, indicates the presence of sulphur or of antimonic oxide.—The pentasulphide dissolves readily in *potash* or *soda-ley*, also in *sulphide of ammonium*. With a solution of sulphate of *copper* or nitrate of *silver*, it forms sulphantimonate of copper or silver, together with antimonic oxide.

SULPHANTIMONATES.—Pentasulphide of antimony is a strong sulphur-acid, uniting readily with the more basic metallic sulphides, and forming sulphur-salts, most of which have the composition $3M^2S.Sb^2S^5$, or M^3SbS^4 [or $3MS.SbS^5$, if $S = 16$], analogous to that of the ordinary tribasic phosphates (M^3PO^4). The sulphantimonates of the alkali-metals and alkaline earth-metals, are very soluble in water, and crystallise for the most part with several atoms of water; none of them appear to be soluble in alcohol. The sulphantimonates of the heavy metals are insoluble in water.

The soluble sulphantimonates are obtained:—1. By fusing pentasulphide of antimony or a mixture of the trisulphide and sulphur, with the sulphide of an alkali-metal, or with charcoal and the carbonate or sulphate of an alkali-metal. If a strong heat is used, the addition of sulphur to the trisulphide is unnecessary, as at high temperatures that compound is resolved into metallic antimony and the pentasulphide.—2. By dissolving pentasulphide of antimony in aqueous solutions of the alkaline hydrosulphates.—3. By dissolving the pentasulphide in the solution of a caustic alkali, or of an alkaline carbonate at the boiling heat; in which process an antimonate of the alkali-metal is formed simultaneously, and deposited as a white powder.—4. By decomposing the aqueous solutions of the alkaline antimonates with hydrosulphuric acid, ⅔ of the antimony being thereby separated as pentasulphide, because the alkaline antimonates are monobasic, and the sulphantimonates tribasic:

$$\begin{array}{lllllllll} & 3(K^2O.Sb^2O^5) & + & 18H^2S & = & 3K^2S.Sb^2S^5 & + & 18H^2O & + 2Sb^2S^5. \\ \text{or:} & 3KSbO^3 & + & 9H^2S & = & K^3SbS^4 & + & 9H^2O & + Sb^2S^5. \end{array}$$

The insoluble sulphantimonates are prepared by gradually adding a solution of a metallic salt to a solution of the sulphantimonate of an alkali-metal, that of sodium being generally used, keeping the latter in excess. If, on the other hand, the solution of the other salt is in excess, and especially if the liquid be boiled, the resulting precipitate contains oxygen, and the liquid is found to contain free acid. The precipitates thus formed generally contain $3M^2S.Sb^2S^5 + 5M^2O$, or rather $8M^2S + Sb^2O^5$, being, in fact, mere mixtures of a metallic sulphide with antimonic oxide, the latter being retained in them by its insolubility. (Rammelsberg. Pogg. Ann. lii. 193.)

The soluble sulphantimonates are decomposed by all acids, even by carbonic acid, with evolution of sulphuretted hydrogen. Many of the insoluble salts are decomposed only by nitric acid and aqua-regia. The sulphantimonates of the alkali-metals are not decomposed by ignition in closed vessels; those of the heavy metals give off sulphur at a red heat, leaving sulphantimonites containing $3M^2S.Sb^2S^3$, or M^3SbS^3.

Sulphantimonate of Ammonium, $3(NH^4)^2S.Sb^2S^5$, or $(NH^4)^3SbS^4$, is produced by digesting pentasulphide of antimony in excess with pure sulphide of ammonium, free from excess of ammonia. It cannot be obtained in the solid state, being decomposed both by concentration, even out of contact with the air, and by mixture with alcohol.

Sulphantimonate of Barium, $Ba^3SbS^4 + 3H^2O$.—Obtained by dissolving recently precipitated prosulphide of antimony in sulphide of barium, and mixing the solution with alcohol, in stellate needles, which, when exposed to the air, do not deliquesce, but become covered with a brown kermes-coloured film.

Sulphantimonate of Bismuth is obtained by precipitation, but is not easily obtained free from excess either of pentasulphide of antimony or of sulphide of bismuth.

Sulphantimonate of Cadmium.—Light orange-coloured precipitate obtained by dropping a neutral cadmium-salt into a solution of sulphantimonate of sodium.

Sulphantimonate of Calcium. Sulpho stibias-calcius. Ca^3SbS^4.—Produced like the barium-salt, but cannot be crystallised. A mixture of this compound with excess of lime and saffron of antimony, constitutes the pharmaceutical preparation known as *Calx antimonii cum sulphure Hoffmanni*, *Sulphuretum stibii cum calce*, or *Calcaria sulphurata stibiata*, discovered by Hoffmann in the eighteenth century. It is prepared by igniting an intimate mixture of 3 pts. trisulphide of antimony, 4 pts. sulphur, and 16 pts. quicklime; or 8 pts. of prepared oyster shells, 1 pt. antimony, and 2 pts. sulphur. It is a whitish-yellow, yellowish, or brownish-yellow powder, which has a sharp sulphurous taste, smells of sulphuretted hydrogen when exposed to moist air, and is but partially soluble in water. The solution is colourless, and contains sulphantimonate of calcium.

Sulphantimonate of Cobalt, obtained by precipitation, is black, oxidises in the air, and is decomposed by boiling hydrochloric acid.

Sulphantimonate of Copper. Cu^3SbS^4.—Obtained by dropping a solution of cupric acetate or sulphate into a solution of sulphantimonate of sodium. The solutions must be rather dilute; the copper-solution must be dropped in slowly and with rapid stirring; and the precipitate then heated, together with the liquid, with brisk stirring all the while. Without these precautions, each drop of the copper-solution, as it enters, becomes enveloped by the precipitate; and if the precipitate be thrown on the filter in this state, the solution of sulphantimonate of sodium runs away first, and then the acetate of copper and sulphantimonate of copper decompose each other, acetic acid or sulphuric acid being set free, which then acts upon the sulphantimonate of sodium still remaining in the precipitate, setting free pentasulphide of antimony and hydrosulphuric acid. In this manner, the precipitate becomes contaminated with pentasulphide of antimony and sulphide of copper.—Sulphantimonate of copper, when pure, is a dark brown precipitate, which when heated gives off sulphur, and leaves a residue apparently consisting of cuprous sulphantimonite (Sb^2S^3 with Cu^4S). Boiling potash decomposes the sulphantimonate, separating sulphide of copper and dissolving pentasulphide of antimony, which is at the same time partially converted into antimonic acid.

If sulphantimonate of sodium be added to excess of cupric sulphate, and the precipitate boiled for some time with the liquid, a product is obtained containing 16 at. copper, 8 at. sulphur, 2 at. antimony, and 5 at. oxygen, and the liquid exhibits a strong acid reaction:

$$3Na^2S.Sb^2S^5 + 8Cu^2SO^4 + 5H^2O = (8Cu^2S + Sb^2O^5) + 3Na^2SO^4 + 5H^2SO^4.$$

The precipitate thus formed, may, as already observed (see above), be either $3Cu^2S.Sb^2S^5 + 5Cu^2O$, or $8Cu^2S + Sb^2O^5$. On boiling it with potash-ley, sulphide of copper remains behind, and a solution of antimonate of potassium is formed, which gives with acids a white precipitate of antimonic acid. On the other hand, the precipitate, when quickly and strongly heated in close vessels, gives off a large quantity of sulphurous anhydride, but no sulphur, and the residue contains sulphide of copper and pentasulphide of antimony. Moreover the same products are obtained by igniting a mixture of 8 at. pure sulphide of copper, and 1 at. pure antimonic oxide, or of 1 at. sulphantimonate of copper and 5 at. cupric oxide. So far then it is impossible to decide upon the constitution of the precipitate obtained in the manner just described. But when sulpharsenate of potassium is dropt into excess of cupric sulphate, and the mixture boiled, a precipitate is obtained consisting of pure sulphide of copper, the whole of the arsenic remaining dissolved as arsenic acid. Hence, from the analogy of the arsenic and antimony compounds, it is probable that the antimony precipitate abovementioned is a mixture of sulphide of copper and antimonic oxide.

Sulphantimonate of Iron.—Ferrous sulphate dropt into sulphantimonate of sodium forms a black precipitate, which quickly turns reddish-yellow. The sodium-salt forms with ammonio-ferric sulphate, so long as the latter is in excess, a greenish-brown precipitate, consisting merely of sulphur and pentasulphide of antimony, the whole of the iron being reduced to the ferrous state and remaining in the liquid.

Sulphantimonate of Lead. Pb^3SbS^4.—Obtained by adding acetate of lead to sulphantimonate of sodium, with the same precautions as those described for the preparation of the copper-salt. It is a dark brown precipitate, which is decomposed by heat, giving off 2 at. sulphur, and leaving sulphantimonite of lead, $3Pb^2S.Sb^2S^3$, or Pb^3SbS^3, of the same composition as the mineral Boulangerite. Boiling potash-ley decomposes it in the same manner as the copper-salt. A precipitate, containing 16Pb, 8S, 2Sb, and 5O, is likewise obtained by adding sulphantimonate of sodium to excess of acetate of lead.

Sulphantimonate of Magnesium.—Recently precipitated pentasulphide of antimony dissolves in aqueous hydrosulphuric acid, in which magnesia is suspended, the magnesia likewise dissolving; but the compound cannot be made to crystallise.

Sulphantimonate of Manganese.—Red-brown precipitate, produced by mixing the sodium-salt with sulphate of manganese; it oxidises during washing and drying.

Sulphantimonates of Mercury.—The *mercuric* salt, $3Hg^2S.Sb^2S^5$, or Hg^3SbS^4, obtained like the copper- and lead-salts, is an orange-coloured precipitate. If after washing it be immersed in solution of mercuric chloride, or a solution of sulphantimonate of sodium be added to excess of mercuric chloride, a white substance is formed, containing $3Hg^2S.Sb^2S^5 + 6HgCl + 3Hg^2O$. This substance is not a mere mixture, but a chemical compound, which is not attacked by any acid except aqua-regia. Potash decomposes it immediately, leaving mercuric sulphide, and dissolving antimonic and hydrochloric acids.—*Mercurous* nitrate, mixed with sulphantimonate of sodium, forms a black precipitate, whichever salt may be in excess.

Sulphantimonate of Nickel.—Black precipitate, which oxidises in the air, and is decomposed by hot hydrochloric acid.

Sulphantimonate of Potassium, K^3SbS^4; in the crystallised state $2K^3SbS^4 + 9H^2O$, or $3K^2S.Sb^2S^5 + 9H^2O$.—The anhydrous salt is obtained by fusing sulphide of potassium with trisulphide of antimony and sulphur, or sulphate of potassium with the trisulphide and charcoal, or by heating one of the potassium-livers of antimony, in which case metallic antimony separates out. The product is a brown mass, the aqueous solution of which yields crystals of the hydrated salt. The latter is, however, better obtained by boiling a mixture of 11 pts. of finely levigated trisulphide of antimony, 6 pts. of carbonate of potassium, 1 pt. of flowers of sulphur, and 3 pts. of lime previously burnt and slaked, with 20 pts. of water, for some hours, renewing the water as it evaporates; or by leaving the same mixture in a covered vessel for 24 hours, and stirring frequently; then filtering and evaporating. The hydrated salt forms colourless or yellowish, granular or radiating crystals, which give off their water when heated.

Sulphantimonate of potassium is likewise formed when pentasulphide of antimony is boiled with aqueous carbonate of potassium, antimonate of potassium being formed at the same time, and separating in the solid state. Hot caustic potash-ley dissolves the pentasulphide completely; but on diluting the solution, and adding carbonate of ammonium, a precipitate is formed, consisting merely of the pentasulphide mixed with a small quantity of sulphantimonate of potassium. Cold potash-ley of moderate strength acts upon pentasulphide of antimony somewhat differently; the pentasulphide loses its colour; white acid antimonate of potassium ($K^2O.2Sb^2O^5 + 6H^2O$) remains undissolved, notwithstanding the excess of potash present; free sulphide of potassium is formed; and the liquid yields by evaporation a colourless double salt, consisting of sulphantimonate and antimonate of potassium ($K^3SbS^4.KSbO^3 + 5H^2O$), crystallising in long needles, which, when exposed to the air, become covered with a kermes-coloured film. Cold water renders these crystals milk-white, dissolving a portion, and leaving a white residue of acid antimonate of potassium. Hot water dissolves the salt readily, and the solution, when mixed with acids, yields an orange-coloured precipitate, consisting of pentasulphide of antimony mixed with antimonic acid.

Sulphantimonate of Silver, Ag^3SbS^4, prepared like the lead- and copper-salts forms a black, perfectly insoluble precipitate, which gives off sulphur when heated, leaving a fused grey residue of sulphantimonate of silver, Ag^3SbS^3, which yields a red powder by trituration.—By adding sulphantimonite of sodium to excess of nitrate of silver and boiling for several hours, a precipitate is obtained containing antimonic oxide, which may be completely extracted from it by potash.

Sulphantimonate of Sodium, $Na^3SbS^4 + 9H^2O$, or $3NaS.SbS^5 + 9HO$. *Schlippe's salt.*—This salt is prepared by digesting at ordinary temperatures in a vessel that can be closed, and with frequent stirring, a mixture of 11 pts. of elutriated trisulphide of antimony, 13 pts. crystallised carbonate of sodium, 1 pt. flowers of sulphur, 5 pts. of quick lime previously slaked, and 20 pts. of water. After twenty-four hours, the liquid is strained off, the residue washed several times with water, and the solution together with the wash-water, is evaporated in a porcelain dish or clean iron pot, till a sample yields crystals on cooling. The whole is then left to cool quietly, and the resulting crystals are washed several times with cold water, and dried in the air, or better, under a bell jar, over lime or oil of vitriol. The formation of the salt is much accelerated by boiling the mixture. (Liebig, Handwört. d. Chem. 2te Aufl. ii. 139. For other modes of preparation, see Gmelin's Handbook, iv. 384.)

Sulphantimonate of sodium forms transparent, colourless, or pale yellow, regular tetrahedrons, with truncated summits, or acuminated with the faces of the rhombic dodecahedron. Its taste is bitterly metallic, and at the same time alkaline. It dissolves in 2·9 pts. of water at 15° C., and the solution is precipitated by alcohol. When heated, it melts in its water of crystallisation, and after all the water has gone off, forms a greyish-white mass, which crumbles to a bulky powder when exposed to the air. At a commencing red heat, it fuses, without decomposition, if the air be excluded. The fused mass is liver-coloured, and dissolves in water, leaving a small quantity of sulphide of antimony. The decomposition of the solution, as well as of the salt itself, by contact with the air, is due to the action of carbonic acid, but is not complete even after many months. The resulting brown precipitate contains sulphantimonate of sodium with trisulphide of antimony, and the liquid is found to contain carbonate, sulphide, and hyposulphite of sodium, but no sulphate.

When sulphantimonate of sodium is added to a solution of tartar-emetic, the liquid first turns red, and then yields an orange-coloured precipitate containing pentasulphide, trisulphide, and trioxide of antimony, while tartrate of sodium and potassium remains in solution:

$$6C^4H^4KSbO^7 + 2Na^3SbS^4 = 6C^4H^4KNaO^6 + Sb^2S^5 + Sb^2S^3 + 2Sb^2O^3$$

This precipitate melts at a high temperature, forming a black metallic-shining mass, exhibiting red translucence on the edges, and perfectly soluble in hydrochloric acid. Potash decomposes it, leaving a yellow residue consisting of sulphide of sodium, trioxide of antimony, and a compound of that oxide with potash. (Handwörterbuch.)

Sulphantimonate of Strontium.—Prepared like the calcium-salt: not crystallisable.

Sulphantimonate of Uranium.—Yellow-brown precipitate, obtained by adding ammonio-uranic chloride to sulphantimonate of sodium.

Sulphantimonate of Zinc, obtained by dropping sulphate of zinc into a solution of the sodium-salt, is an orange-coloured precipitate which dissolves in the liquid when heated, and partly runs through the filter during washing. It is decomposed and dissolved by hydrochloric acid.

The precipitate obtained with excess of the zinc-salt, has the same colour, but is not easily obtained free from the preceding, even after long boiling. Fuming nitric acid decomposes it, with ignition. (Handwörterbuch.)

ANTIMONY, SULPHOCHLORIDE OF. $SbSCl^3$. Obtained by slowly passing dry sulphuretted hydrogen into pentachloride of antimony. It is a white crystalline body, which melts at a moderate heat, is resolved at a higher temperature into sulphur and trichloride of antimony, deliquesces in moist air, and is decomposed by water into sulphur and trichloride (? oxychloride) of antimony; with aqueous tartaric acid, it yields a precipitate of sulphide of antimony mixed with oxide. (Cloez, Ann. Ch. Phys. [3] xxx. 374.)

Other sulphochlorides of antimony have been obtained by R. Schneider (Pogg. Ann. cviii. 407). Finely pulverised trisulphide of antimony dissolves in 14 or 15 times its weight of the melted trichloride, without evolution of sulphuretted hydrogen, and the light brown solution solidifies on cooling to a yellow crystalline mass. By pouring off the still remaining liquid at a certain stage of the solidification, the compound may be obtained in regular crystals (rhombic prisms bevelled at the ends with a macrodiagonal dome), containing $Sb^2SCl^4.6SbCl^3$. It is very deliquescent, and is decomposed by a large quantity of water, with separation of a yellow powder; by prolonged heating, it is resolved into volatile trichloride of antimony, and a black residue of sulphide. It is decomposed by absolute alcohol, out of contact of air, a large quantity of chloride of antimony and a little of the sulphide dissolving, and a reddish-yellow amorphous substance being left, containing $2SbClS.3Sb^2S^3$. This compound is decomposed, by heating in close vessels, into trichloride and trisulphide of of antimony, also by the action of dilute hydrochloric acid.

ANTIMONY, SULPHIODIDE OF. SbSI.—This compound is obtained by dissolving trisulphide of antimony in the melted tri-iodide. It has a brilliant metallic lustre and red-brown colour, appears red and transparent under the microscope, and yields a powder of a fine cherry-red colour. (R. Schneider, J. pr. Chem. lxxix. 422; Rép. Chim. pure, ii. 323.)

When a mixture of equal parts of iodine and trisulphide of antimony is slowly heated in a retort, an iodosulphide, probably of the same composition, rises in red vapours, which condense in the receiver. The same body is formed by subliming a mixture of 24 pts. antimony, 9 pts. sulphur, and 68 pts. iodine, or of 2 pts. iodine and 9 pts. iodide of sulphur. It forms shining transparent, blood-red needles and laminæ, which melt at a gentle heat, and sublime more easily than the iodide of antimony. It has a pungent taste and repulsive odour. It is decomposed at a strong heat, also by chlorine and by water. Henry and Garot (J. Pharm. x. 511), assigned to this product the formula SbS^2I^2; but this is doubtless incorrect.

ANTIMONY-RADICLES, ORGANIC. Antimony combines with alcohol-radicles in various proportions, forming compounds which themselves act like simple radicles, uniting with chlorine, oxygen, sulphur, &c., in the same manner as the metals. Some of these bases are formed on the type of ammonia, NH^3, containing 1 at. antimony united with 3 at. of the alcohol-radicle; others on the type NH^4; and a compound of antimony with amyl is known containing 1 at. antimony with 2 at. amyl. The names and formulæ of the antimony-radicles at present known, are given in the following table: —

Antimonides of Amyl:	
Stibdiamyl	$Sb(C^5H^{11})^2$
Stibtriamyl *or* Triamylstibine	$Sb(C^5H^{11})^3$
Antimonides of Ethyl:	
Stibtriethyl *or* Triethylstibine	$Sb(C^2H^5)^3$
Stibethylium *or* Tetrethylstibonium	$Sb(C^2H^5)^4$
Antimonides of Methyl:	
Stibtrimethyl *or* Trimethylstibine	$Sb(CH^3)^3$
Stibmethylium *or* Tetramethylstibonium	$Sb(CH^3)^4$

The existence of pentethylstibine $Sb(C^2H^5)^5$ and pentamethylstibine $Sb(CH^3)^5$, has also been rendered probable by the recent experiments of Mr. Buckton (Chem. Soc. Qu. J. xiii. 115).

The compounds containing 3 at. of alcohol-radicle are obtained by distilling the iodides of the alcohol-radicles with antimonide of potassium or sodium, or by the action of trichloride of antimony on zinc-ethyl. They are liquids which volatilise without decomposition, and rapidly absorb oxygen from the air, with great evolution of heat, sufficient in the case of the ethyl- and methyl-compounds to produce vivid combustion. The compounds containing 4 at. of alcohol-radicle are not known in the free state; but their iodides are obtained by treating the corresponding compounds containing 3 at. alcohol-radicle with the iodides of those radicles; and these iodides when treated with oxide of silver and water, yield the hydrated oxides of the same radicles, which are fixed bases, having a strong alkaline reaction, and uniting readily with acids like the hydrates of potassium and sodium. In this respect, they resemble the corresponding nitrogen-bases, hydrate of tetrethylium, $N(C^2H^5)^4.H.O$, &c.

The antimony-radicles containing 4 at. of the alcohol-radicle, are monatomic, uniting with 1 at. chlorine, iodine, &c.; but those which contain 3 at. alcohol-radicle, stibtriethyl, for example, are diatomic, uniting with 2 at. chlorine, iodine, &c., and with 1 at. oxygen, *e.g.* $Sb(C^2H^5)^3.Cl^2$, $Sb(C^2H^5)^3O$, &c. The same law holds good with respect to other organo-metallic bodies similarly constituted, arsentriethyl, for example: but it does not extend to the corresponding nitrogen-radicles, such as triethylamine, trimethylamine, &c., which, indeed, do not unite directly with oxygen, chlorine, iodine, &c., but combine with hydrated acids in the same manner as ammonia.

Antimonides of Amyl, or Stibamyls.*

These compounds are obtained by the action of iodide of amyl on antimonide of potassium, the process being conducted similarly to that for the preparation of stibethyl (p. 341). After the action has ceased, and the excess of iodide of amyl has distilled off, the residue is either distilled in an atmosphere of carbonic anhydride, whereby a distillate is obtained containing stibdiamyl; or the product is exhausted with ether, and the solution freed from ether by distillation, in which case a residue is left consisting of stibtriamyl. If the stibtriamyl thus obtained is contaminated with amylic alcohol or iodide of amyl, pure compounds may be prepared from it by dissolving it in a mixture of ether and alcohol; adding alcoholic bromine till its colour just begins to be permanent; precipitating the bromide of stibtriamyl by adding a large quantity of water; converting the bromide into oxide by means of oxide of silver suspended in

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* F. Berlé, J. pr. Chem. lxv. 385; Gm. xi. 125.

alcohol; precipitating the oxide by water, and dissolving it in hydrochloric acid and alcohol; precipitating the pure chloride by another addition of water; and freeing it from a small quantity of water by heating it to 100° C. in contact with fused chloride of calcium.

STIBDIAMYL. $Sb(C^5H^{11})^2 = SbAm^2$. — The distillate just mentioned, after being freed from undecomposed iodide of amyl by re-distillation over antimonide of potassium, gave off at 80° C. a colourless liquid, which burnt with a white flame, diffusing a white smoke of oxide of antimony. The liquid which then remained was stibdiamyl. It was greenish-yellow, heavier than water, and tolerably mobile, with a peculiar aromatic odour and bitter taste; insoluble in water, but miscible in all proportions with alcohol and ether. It was not spontaneously inflammable, but when set on fire, burned with a very white flame, diffusing a white fume of oxide of antimony. It exploded with great violence when heated in oxygen gas, and was decomposed by nitric acid with considerable evolution of heat. Its ethereal solution exposed to the air, left an oxide which absorbed carbonic acid; and the stibdiamyl itself heated to 100° C. in a stream of dry carbonic acid, yielded a viscid liquid, which appeared to be the carbonate $(SbAm^2)^2.CO^3$. The haloïd salts of stibdiamyl are gummy liquids; the sulphate and nitrate are precipitated from their alcoholic solutions by water, in the form of gummy masses, which dry up to amorphous solids.

STIBTRIAMYL OF TRIAMYLSTIBINE. $Sb(C^5H^{11})^3 = SbAm^3$.—Transparent slightly yellowish liquid, very viscid below 20° C., more mobile at higher temperatures. It has a peculiar aromatic odour, and a bitter, somewhat metallic and very persistent taste. Specific gravity 1·333 at 17° C. (according to Cramer, Pharm. Centr. 1855, 465, it is 1·0587). In contact with the air, it does not take fire, but fumes strongly and decomposes, depositing a white powder. A drop of it placed on bibulous paper and exposed to the air, becomes so strongly heated as to char the paper. It is insoluble in water, but dissolves sparingly in alcohol, and readily in ether. It does not exhibit any tendency to unite with iodide of amyl, when heated with that compound in a sealed tube.

Stibtriamyl is a diatomic radicle, like stibtriethyl. Its *oxide*, $Sb(C^5H^{11})^3.O =$ is produced by slow evaporation of an ethereal solution of stibtriamyl in contact with the air; or by decomposing the chloride, iodide, or bromide with oxide of silver. It is a greyish-yellow viscid mass, which becomes somewhat more fluid when gently heated, but decomposes at higher temperatures. It tastes and smells like the radicle itself. It is insoluble in water, sparingly soluble in dilute alcohol and in ether, but dissolves easily in absolute alcohol. The alcoholic solution precipitates metallic oxides from their salts. Oxide of stibriamyl dissolves readily in acids, and the resulting compounds are precipitated from their solutions by water.

1. The *chloride*, $Sb(C^5H^{11})^3Cl^2$, obtained by dissolving the oxide in hydrochloric acid, is a yellowish translucent liquid, viscid at ordinary, comparatively mobile at higher temperatures, heavier than water, soluble in alcohol and ether. It tastes and smells like stibtriamyl. Decomposes at temperatures above 160° C. The *bromide* and *iodide* resemble the chloride.

Nitrate. $Sb(C^5H^{11})^3.2NO^3$.—When the chloride or iodide is mixed with an alcoholic solution of nitrate of silver, as long as a precipitate forms, and then filtered, the filtrate forms an emulsion, from which, after standing for some time in a warm place, two liquids separate, the upper being light, yellow, and mobile, and the lower a deep brown-red oil. The upper layer, when slowly evaporated, yields the nitrate in slender white crystals grouped in stars; they may be purified by recrystallisation from dilute alcohol. The dark red oil likewise dissolves on addition of a large quantity of hydrated alcohol, and the solution, after standing for some time, yields the same crystals. These crystals melt at about 20° C.: the fused mass does not dissolve in alcohol so readily as the crystals. This salt, the only crystallisable compound of stibtriamyl, is insoluble in water and ether, but dissolves in hydrated alcohol. It has a peculiar metallic taste.

The *sulphate*, $Sb(C^5H^{11})^3.SO^4$, is formed by decomposing equivalent quantities of sulphate of silver and a haloïd compound of stibtriamyl dissolved in alcohol. This salt was obtained only as an oily liquid body.

The white powder, formed by the action of the air upon stibtriamyl is insoluble in ether, alcohol, and water: it does not dissolve in hydrochloric acid, but imperfectly in fuming nitric acid; slowly in aqua-regia. It remains unaltered even when strongly heated, not decomposing below a red heat. Berlé supposes it to be *antimonite of stibtriamyl*, $SbAm^3O.Sb^2O^3$. When sulphuretted hydrogen was passed for some time through this compound suspended in alcohol, a white powder immediately separated, which gradually assumed an orange colour, and then formed a pulpy mass, which could not be filtered. After addition of a large quantity of alcohol and ether the liquid, when left to stand in a warm place, deposited an orange-red, flocculent precipitate, which, after drying, formed a brownish-yellow powder, insoluble in alcohol, ether, and water; this powder decomposed at a very high temperature, and took fire when fuming nitric acid was poured upon it. Berlé regards this compound as *sulphantimonite of stibtriamyl*, $SbAm^3S.Sb^2S^3$ (it gave 18·38 per cent. sulphur, the formula requiring 17·59). A compound, supposed to be identical with this, is formed by passing sulphuretted hydrogen for some time through an alcoholic solution of oxide of stibtriamyl.

Antimonides of Ethyl, or Stibethyls.

STIBTRIETHYL OR TRIETHYLSTIBINE, commonly called *Stibethyl*. $Sb(C^2H^5)^3 = SbE^3$. (Löwig and Schweizer, Ann. Ch. Pharm. lxxv. 315, 327; Löwig, *ibid.* lxxx. 323; Gm. ix. 79; Gerh. ii. 370.)—This compound is prepared by the action of iodide of ethyl on antimonide of potassium. The alloy is finely pulverised together with two or three times its weight of quartz-sand (if pulverised alone it is apt to take fire); the mixture is introduced into a number of small short-necked flasks, so as to fill them to about two-thirds; and iodide of ethyl is added in quantity just sufficient to moisten the mixture of alloy and sand. The action begins in a few minutes, and is accompanied with a rise of temperature sufficient to volatilise the excess of iodide of ethyl, which is collected by itself in a small receiver; as soon as this action is over, the flask is connected as quickly as possible with a condensing apparatus, through which a stream of carbonic acid gas is passed during the whole operation. This condensing apparatus consists of a tall wide cylindrical vessel closed by a cork having three apertures. Through one of these apertures, passes a tube proceeding from the carbonic acid apparatus, and reaching to the bottom of the vessel; through the second a short straight tube to carry off that gas, and through the third is inserted the distillation tube connected with the flask containing the mixture: this tube descends nearly to the bottom of the glass cylinder, and drops into the mouth of a small receiver, partly filled with antimonide of potassium. This apparatus being completely filled with carbonic acid gas, the generating flask is heated very gently at first, and afterwards more strongly as long as any liquid distils over. This flask is then removed, the distillation-tube stopped with wax, till a second flask is ready to be adapted, and the operation is then repeated. The contents of 20 to 24 flasks of 3 or 4 ounces capacity yield 4 or 5 ounces of crude product, which may thus be obtained in the course of a day. The receiver in which the distillate has been collected is then closed while still immersed in the atmosphere of carbonic acid, afterwards removed, and used as a retort in the rectification of the product, the same condensing apparatus being used as before. The first portions of the rectified product contain iodine, and deposit after a while, a number of colourless crystals consisting of iodide of stibethylium. (Löwig and Schweizer.)

2. By the action of trichloride of antimony on zinc-ethyl, similarly to the preparation of triethylphosphine. (Hofmann: See PHOSPHORUS BASES.)

Properties. Stibtriethyl is a transparent, colourless, mobile, strongly refracting liquid, having a disagreeable alliaceous odour. Specific gravity 1·3244 at 16° C. It does not solidify at 29° C. Boils at 158°·5 (bar. at 730 mm.). Vapour-density, by experiment = 7·44; by calculation 7·18, the formula $Sb(C^2H^5)^3$, representing 2 volumes of vapour. Stibtriethyl is insoluble in water, but dissolves readily in alcohol and ether.

A drop of stibtriethyl exposed to the air at the end of a glass rod, emits thick white fumes, and in a few seconds takes fire and burns with a white, strongly luminous flame. When introduced in a thin stream into oxygen gas, it burns with dazzling brightness. But if it be made to run into a glass globe containing air, in such a manner as not to take fire, it gives off dense white fumes, which collect on the sides of the vessel in the form of a powder, which is insoluble in ether, but dissolves in alcohol and water; at the same time a transparent, colourless, viscid mass is formed, which is soluble in ether. This latter substance is the *oxide of stibtriethyl*, SbE^3O; the powder is *antimonite of stibtriethyl*, $SbE^3O.Sb^2O^3$. Stibtriethyl oxidises very slowly when immersed in water; hence it is best to keep it under that liquid. *Sulphur, selenium, iodine, bromine*, and *chlorine* combine directly with stibtriethyl, the action being always attended with evolution of heat, and in the case of bromine and chlorine, with inflammation. The compounds contain 1 at. stibtriethyl, with 1 at. of a dibasic radicle, O, S, SO^4 &c., or 1 at. stibethyl with 2 at. of a monobasic radicle, Cl, Br, NO^3, &c., in which respect they resemble the compounds of stibtrimethyl, arsentriethyl (see p. 322). Stibtriethyl introduced into *hydrochloric acid gas*, yields chloride of stibtriethyl and free hydrogen:

$$SbE^3 + 2HCl = SbE^3Cl^2 + H^2.$$

The same reaction takes place with fuming hydrochloric acid. Dilute *nitric acid*, with the aid of heat, acts on stibtriethyl in the same manner as on the metals, evolving nitric oxide and forming nitrate of stibtriethyl. Neither fuming nitric acid nor aqua-regia oxidises the antimony completely.

Antimonite of Stibtriethyl, $Sb(C^2H^5)^3.Sb^2O^4$, or $SbE^3O.Sb^2O^3$, is formed, together with the oxide, by the gradual oxidation of stibtriethyl. The white fumes which stibtriethyl diffuses in the air consist almost wholly of this compound. It may be prepared by leaving an ethereal solution of stibtriethyl to evaporate spontaneously, and dissolving out the simultaneously formed oxide with ether-alcohol. The antimonite then remains as a white, pulverulent, amorphous body. It has a bitter taste, and is soluble in water and in alcohol. The aqueous solution prepared in the cold is perfectly mobile, but when heated, becomes viscid like starch-paste, and dries up to a friable mass, having the appearance of porcelain. Water poured upon this mass dissolves the greater part, but leaves a small residue of antimonious oxide. Hydrochloric acid, added to the alcoholic solution throws down chloride of stibtriethyl; the acid liquid separated from the chloride yields with sulphuretted hydrogen, a precipitate of kermes; on mixing it with water, powder of algaroth is precipitated. (Löwig.)

Bromide of Stibtriethyl. $Sb(C^2H^5)^3Br^2$. —Stibtriethyl takes fire when added by drops to bromine. The bromide is prepared by adding a recently prepared alcoholic solution of bromine to an alcoholic solution of stibtriethyl cooled by ice, as long as the colour of the bromine disappears. On mixing the solution with a large quantity of water, the bromide of stibtriethyl is precipitated, in the form of a colourless liquid which must then be washed with water and dried by contact with chloride of calcium. Transparent, colourless, strongly refracting liquid, having a density of 1·953 at 17° C. Has an unpleasant odour like that of turpentine, and excites sneezing. Solidifies in a crystalline mass at − 10° C. It is not volatile. When distilled, it yields, among other products a strongly acid liquid having an intolerable odour like that of chloral. It is decomposed by oil of vitriol, with evolution of hydrobromic acid, and by chlorine with separation of bromine. Insoluble in water, but dissolves readily in alcohol and ether. The alcoholic solution gives with metallic salts, reactions similar to those of bromide of potassium.

Chloride of Stibtriethyl. $Sb(C^2H^5)^3Cl^2$.—Stibtriethyl dropt into chlorine gas takes fire and burns with a bright but smoky flame. Introduced into dry hydrochloric acid gas, it forms chloride of stibtriethyl, and separates a quantity of hydrogen equal in volume to half the hydrochloric acid gas. The chloride is easily obtained in the pure state by decomposing a strong solution of nitrate of stibtriethyl with strong hydrochloric acid; it then separates in the form of a liquid which may be purified in the same manner as the bromide. Transparent, colourless liquid, of specific gravity 1·540 at 17° C.; it has a powerful odour like that of turpentine, and a bitter taste. Remains fluid at 12° C. When it is distilled with water, a small portion appears to volatilise undecomposed; when heated alone, it behaves like the bromide. Strong sulphuric acid decomposes it, with evolution of hydrochloric acid, while, on the other hand, hydrochloric acid added to a solution of sulphate of stibtriethyl throws down the chloride. In other respects, its relations are like those of chloride of potassium or chloride of sodium. It is insoluble in water, but dissolves readily in alcohol and ether.

Cyanide of Stibtriethyl appears to be formed when 2 at. cyanide of mercury, and 1 at. sulphide of stibtriethyl are mixed in the state of aqueous solution. Sulphide of mercury is then formed, together with a liquid which smells like prussic acid, and behaves with metallic salts like cyanide of potassium.

Iodide of Stibtriethyl. $Sb(C^2H^5)^3I^2$.—Iodine and stibtriethyl combine together under water, with rise of temperature. On adding iodine to an ethereal solution of stibtriethyl, a violent momentary ebullition takes places, and the iodine quickly disappears. The iodide is, however, most easily prepared by adding iodine in small portions to an alcoholic solution of stibtriethyl surrounded by a frigorific mixture, as long as the colour of the iodine disappears, and leaving the colourless solution to evaporate. The iodide then crystallises in colourless needles, which must be recrystallised from alcohol, and afterwards from ether, to free them from a small quantity of adhering yellow powder.

Iodide of stibtriethyl has a slight odour of stibtriethyl and a bitter taste. It dissolves in water without decomposition and readily in alcohol and ether. It melts and solidifies at 70°·5 C., sublimes in small quantity at 100°, without alteration, but is decomposed at a somewhat higher temperature, with formation of dense white fumes. In the fused state, it is instantly decomposed by *potassium*, with separation of stibtriethyl. With *sulphuric acid* and with metallic salts, it behaves like iodide of potassium. *Hydrochloric acid* immediately precipitates chloride of stibtriethyl. *Bromine* and *chlorine* separates the iodine; so likewise does nitric acid, forming nitrate of stibtriethyl. With *zinc-ethyl* it appears to form stibpentethyl, $SbE^3I^2 + ZnE = 2ZnI + SbE^5$; but this compound is decomposed by distillation into stibtriethyl, ethylene, and hydride of ethyl; $Sb(C^2H^5)^5 = Sb(C^2H^5)^3 + C^2H^4 + C^2H^6$. (**Buckton**, Chem. Soc. Qu. J. xiii. 116.)

Oxyiodide of Stibtriethyl. $(SbE^3)^2I^2O = SbE^3I^2,SbE^3O$.—Produced by the action of ammonia on iodide of stibtriethyl:

$$2SbE^3I^2 + 2NH^3 + H^2O = (SbE^3)^2I^2O + 2NH^4I$$

also by mixing the oxide and iodide of stibtrethyl in equivalent quantities. It forms octahedral crystals containing 36·9 per cent. iodine: by calculation 37·1 (**Strecker** Ann. Ch. Pharm. cvi. 306). Merck, who obtained this compound by mixing iodide of stibtriethyl with an ethereal solution of stibtriethyl in an atmosphere of carbonic anhydride, supposed it to be, not an oxyiodide, but a monoiodide of stibtriethyl SbE^3I, and explained its formation, together that with of another crystalline compound — not analysed, but supposed to be SbE^3HI,—on the hypothesis that the iodide of stibtriethyl prepared by Löwig and Schweizer, really contained 1 at. hydrogen more than those chemists supposed, its true formula being SbE^3HI^2, or $SbE^3I.HI$:

$$SbE^3HI^2 + SbE^3 = SbE^3I + SbE^3HI.$$

But the formula $SbE^3.I$ is contrary to analogy, the triethyl- and trimethyl-compounds of arsenic, bismuth, and phosphorus, all uniting with 2 at. I, Br or Cl. Moreover Merck's mode of preparation, which consisted in covering the liquid with a funnel, and passing a stream of carbonic anhydride through the beak, till all the ether was evaporated, was not very well adapted to exclude the air perfectly; hence it is probable, especially as the action took place but slowly, that oxide of stibtriethyl was first formed, and then combined with the iodide. The oxyiodide might, however, be formed without access of air, if the mixture was not perfectly dry, the compound SbE^3HI being produced at the same time: thus,

$$2SbE^3 + 2SbE^3I^2 + H^2O = (SbE^3)^2I^2O + 2SbE^3HI$$

The oxyiodide treated with hydriodic acid yields iodide of stibtriethyl and water:

$$(SbE^3)^2I^2O + 2HI = 2SbE^3I^2 + H^2O$$

With oxide of silver, it yields oxide of stibtriethyl, SbE^3O, and with chloride of mercury, an oxychloride of stibtriethyl, $(SbE^3)^2Cl^2O$. (**Strecker.**)

Merck supposed that the action of various mercury and silver-salts on his supposed iodide, SbE^3I, yielded a series of compounds of analogous constitution, viz. a chloride, SbE^3Cl, an oxide $(SbE^3)^2O$, &c.

Nitrate of Stibtriethyl. $Sb(C^2H^5)^3.2NO^3$.—Obtained by saturating dilute nitric acid with oxide of stibtriethyl, or by dissolving stibtriethyl in the dilute acid with the aid of heat. In this latter reaction, nitric oxide is evolved, and a small quantity of antimonious oxide separates. The salt may be obtained in crystals by evaporating the solution. At 62°·5 C. it melts into a transparent liquid, which solidifies to a crystalline mass at 57°; at a higher temperature, it deflagrates like a mixture of nitre and charcoal. It dissolves easily in water, less easily in alcohol, and is nearly insoluble in ether. The solutions have an acid reaction and bitter taste.

Oxide of Stibtriethyl. $Sb(C^2H^5)^3O$.—Formed by the direct oxidation of stibtriethyl, either in the free state, as above mentioned, or dissolved in alcohol or ether; as thus obtained, however, it is always more or less mixed with antimonite of stibtriethyl, especially when obtained from the ethereal solution. The alcoholic solution on the contrary yields but a small quantity of antimonite. Accordingly, the oxide may be obtained by leaving a dilute alcoholic solution to evaporate slowly in a loosely covered foot-glass, treating the residue with ether, which dissolves the oxide and leaves the antimonite, and repeating this treatment as long as the ether leaves any insoluble residue.—The oxide may also be obtained by treating an aqueous solution of sulphate of stibtriethyl with baryta-water; evaporating the filtrate over the water-bath; exhausting the residue with alcohol, which dissolves out a compound of oxide of stibtriethyl and baryta; precipitating the baryta by carbonic acid, and evaporating the filtered alcoholic solution. An alcoholic solution of stibtriethyl shaken up with finely divided red oxide of mercury, quickly reduces the mercury to the metallic state, and yields pure oxide of stibethyl.

Oxide of stibtriethyl in its purest state, is a transparent, colourless, viscid, amorphous mass, which dissolves readily in water and alcohol, somewhat less readily in ether; has a very bitter taste; does not appear to be poisonous; is not altered by exposure to the air; is not volatile; but when heated in a tube, gives off white vapours which burn with a bright flame, and leaves a residue containing antimony and charcoal. It is decomposed by *potassium*, at a gentle heat, with separation of stibtriethyl. *Fuming nitric acid* decomposes it, with evolution of light and heat; *dilute nitric* and *strong sulphuric acid* dissolve it, forming salts of stibtriethyl; *hydrochloric acid* and other hydrogen-acids dissolves it in the form of chloride of stibtriethyl and similar compounds.

Hydrosulphuric acid has no perceptible action upon it; but on evaporating a solution of the oxide saturated with the gas, crystals of sulphide of stibtriethyl are obtained; the smallest trace of antimonite of stibtriethyl mixed with the oxide is detected by the formation of a yellow precipitate.

Sulphate of Stibtriethyl, $Sb(C^2H^5)^3.SO^4$, is obtained by decomposing the aqueous solution of the sulphide with sulphate of copper. It crystallises in small white prisms, soluble in water and alcohol, inodorous, but having a bitter taste and acid reaction.

Sulphide of Stibtriethyl, $Sb(C^2H^5)^3S$, is formed, with evolution of heat, when sulphur and stibtriethyl are brought together under water. But it is most readily obtained by boiling an ethereal solution of stibtriethyl with flowers of sulphur; the liquid decanted from the sulphur soon solidifies in needle-shaped crystals, which may be purified by leaving the adhering sulphur to oxidise in the air, and crystallising several times from ether. Sulphide of stibethyl thus purified forms a bulky mass, having a silvery lustre, an unpleasant odour, and a bitter taste; it is permanent in the air when dry, melts above 100° C., and is decomposed by a stronger heat, with evolution of stibtriethyl vapour. The aqueous solution of the sulphide precipitates metals from their solutions as sulphides, and yields sulphuretted hydrogen with dilute acids.

Sulphantimonite of Stibtriethyl. $SbE^3.Sb^2S^4$, or $SbE^3S.Sb^2S^3$. — Sulphuretted hydrogen passed through a solution of the antimonite, throws down this compound in the form of a light yellow precipitate, having an extremely unpleasant, persistent odour, like that of mercaptan. The compound is also formed by adding recently precipitated trisulphide of antimony to a solution of sulphide of stibtriethyl, the latter being in excess, whereupon the brown-red colour of the kermes immediately changes to light yellow. Dried over sulphuric acid, it forms a powder of a beautiful light yellow colour, which changes to brown-red at the heat of the water-bath. When distilled over a spirit-lamp, it yields a liquid distillate having all the properties of sulphide of stibtriethyl. Dilute sulphuric acid poured upon it, separates trisulphide of antimony, with evolution of sulphuretted hydrogen, and formation of sulphate of stibtriethyl:

$$SbE^3.Sb^2S^4 + SO^4H^2 = SbE^3.SO^4 + H^2S + Sb^2S^3.$$

Fuming nitric acid decomposes it, with emission of light and heat.

STIBETHYLIUM. $Sb(C^2H^5)^4 = SbE^4$. (R. Löwig, J. p. Chem. lxiv. 415; Chem. Soc. Qu. J. viii. 261; Gm. x. 527.) — The iodide of this radicle is formed by introducing a mixture of equal parts of stibtriethyl and iodide of ethyl into a retort filled with carbonic acid gas, nearly filling the retort with water, sealing the neck, and then heating it in boiling water. The solution evaporated and cooled, yields beautiful hexagonal prisms, often an inch long, containing $2SbE^4I.3H^2O$, and other crystals, containing $4SbE^4I.3H^2O$. The salt has a very bitter taste, and 1 pt. of it dissolves in 5·26 pts. of water at 20° C. It dissolves more easily in absolute alcohol, but less in ether. The solution of this salt, mixed with chloride of mercury, forms a white precipitate, which dissolves in warm water, and yields crystals containing $3HgI.SbE^4I$. Another double iodide, $3HgI.2SbE^4I$, is obtained by adding iodide of mercury to a hot solution of iodide of stibethylium.

The iodide digested with oxide of silver, yields a strongly alkaline solution, which when evaporated, leaves the *hydrate of stibethylium* in the form of a thick colourless oily liquid, having a strong alkaline taste and reaction. It expels ammonia from its compounds, precipitates metallic oxides, and redissolves alumina and stannic oxide. It dissolves in acids, forming salts which have a bitter taste. The *carbonate* is a tough deliquescent mass. The *sulphate* and *nitrate* crystallise. The *formate* yields needle-shaped crystals, difficult to dissolve. The *acetate* forms similar crystals, but more soluble. The *oxalate* crystallises; the succinate does not. The neutral *tartrate* and *racemate* form large deliquescent crystals; the acid tartrate, fine needles.

The *sulphide*, $(SbE^4)^2S$, is obtained by treating the oxide with hydrosulphuric acid. It is a yellowish oily liquid, soluble in water and alcohol, and exhibiting the reactions of alkaline sulphides.—The *bromide* and *chloride* are crystalline compounds obtained by saturating the oxide with the corresponding acids. The chloride forms with chloride of mercury, compounds analogous to the double iodides above mentioned. It also combines with dichloride of platinum, producing the compound $3PtCl^2.2SbE^4Cl$, which forms fine yellow crystals, soluble in water and alcohol.

Antimonides of Methyl.[*]

STIBTRIMETHYL. $Sb(CH^3)^3 = SbMe^3$.—Produced, like the corresponding ethyl-compound, by the action of iodide of methyl on antimonide of potassium. It is a colourless heavy liquid, insoluble in water, sparingly soluble in alcohol, readily in ether. When exposed to the air, it gives off thick white fumes, and takes fire, burning with a white

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[*] Landolt, Ann. Ch. Pharm. lxxviii. 91; Gm vii. 321; Gerh. i. 646.

flame and depositing metallic antimony. Its compounds are precisely analogous to those of stibtriethyl.

Stibpentamethyl, $Sb(CH^3)^5$, appears to be produced by the action of zinc-ethyl on stibtrimethyl; and to be decomposed by distillation into stibtrimethyl and hydrocarbons. (Buckton, compare page 336.)

STIBMETHYLIUM. $Sb(CH^3)^4 = SbMe^4$.—This compound is obtained as an iodide by the action of iodide of methyl on stibtrimethyl. It is not quite certain whether it has yet been isolated. The iodide distilled with excess of antimonide of potassium, in an atmosphere of carbonic anhydride, yields a spontaneously inflammable oily liquid, resembling stibtrimethyl; and the aqueous solution of the iodide subjected to the action of the electric current, yields iodine at the positive pole, while at the negative pole, the liquid becomes alkaline, and gives off a spontaneously inflammable gas containing antimony, and having the odour of stibtrimethyl; but which of these products, if either, is stibmethylium, has not yet been ascertained.

The compounds of stibmethylium closely resemble the corresponding potassium-salts, and are isomorphous with them. They have a bitter taste. They are decomposed by potash or soda, and then form white fumes, if a glass rod moistened with hydrochloric acid is held over them. They are for the most part easily soluble in water, less soluble in alcohol, and insoluble in ether. The antimony in them is scarcely recognisable by the ordinary reagents, not being precipitated by hydrosulphuric acid till after a long time. They yield a slight deposit of antimony, when treated with zinc and sulphuric acid in Marsh's apparatus. They bear a heat of about 140° C. without decomposition, but between 180° and 200° they are decomposed, and give off spontaneously inflammable vapours.

Bromide. $SbMe^4Br$.—Obtained by decomposing iodide of stibmethylium with bromide of mercury. On filtering from the iodide of mercury and evaporating, a beautiful salt is obtained, soluble in alcohol and water, but insoluble in ether, and having a saline bitter taste. This compound, when heated, evolves white vapours which take fire in the air. Oil of vitriol poured upon it liberates hydrobromic acid; nitric acid separates bromine. With metallic salts, bromide of stibmethylium behaves in the same manner as bromide of potassium.

Carbonates.—The neutral carbonate is obtained by decomposing a solution of the iodide with recently precipitated carbonate of silver. The filtered liquid evaporated over the water-bath, leaves an indistinctly crystallised, somewhat yellowish, transparent mass, which deliquesces very readily in the air, exhibits an alkaline reaction, dissolves very easily in water and in alcohol, but very slowly in ether. This compound is very unstable, beginning to smell of stibtrimethyl as soon as it is formed. When heated, it gives off white fumes, which take fire spontaneously in the air. It does not appear to contain water of crystallisation.—The *acid carbonate*, $(SbMe.H.)CO^3$, is formed by passing carbonic anhydride through a solution of the oxide or of the neutral carbonate, and evaporating. It crystallises with difficulty in small deliquescent needles, arranged in stars. In the solid form, it soon decomposes, like the neutral carbonate. The aqueous solution evolves carbonic anhydride when heated, and does not precipitate magnesium-salts.

Chloride. $SbMe^4Cl$.—Obtained by adding a hot solution of corrosive sublimate to aqueous iodide of stibmethylium, as long as a precipitate of iodide of mercury is produced. The filtered liquid evaporated over the water-bath deposits the chloride in white six-sided tables, similar to those of the iodide. These crystals are easily soluble in water and alcohol, nearly insoluble in ether: their taste is saline and bitter. This salt intumesces when heated in a tube, and at a higher temperature gradually disappears, giving off white fumes, which take fire spontaneously in the air, and deposit on the cooler part of the tube a white sublimate containing chloride of antimony.

Chloroplatinate. $SbMe^4Cl.PtCl^2$.—Obtained as a yellow crystalline precipitate, by adding dichloride of platinum to chloride of stibethylium. It may be dissolved in boiling water, and separates on cooling as an orange-yellow crystalline powder. It is the least soluble in water of all the salts of stibmethylium, and is intermediate in solubility between the chloroplatinates of potassium and sodium. It is quite insoluble in alcohol and ether, very difficult of solution in alkalis, but dissolves more easily in hot hydrochloric acid. When heated, it turns black, and soon takes fire, leaving an alloy of platinum and antimony, from which the latter metal is but imperfectly removed by aqua-regia.

Hydrate. $SbMe^4.H.O$.—Obtained by agitating an aqueous solution of the iodide with recently precipitated oxide of silver, filtering from the resulting iodide of silver, and evaporating the filtrate in vacuo over sulphuric acid. It is a white, crystalline mass which feels soapy between the fingers, is highly caustic, and dissolves rapidly in water and alcohol, but is insoluble in ether. In the state of aqueous solution, it is slightly volatile, and forms white fumes when a glass rod moistened with hydrochloric acid is held over it; but the solution, when evaporated over the water-bath, yields the original quantity with scarcely any loss. When the solid hydrate is suddenly heated in a test-tube, it gives off vapours which take fire on coming in contact with the air, and deposit metallic antimony; but when carefully heated, it sublimes undecomposed.

The aqueous solution has an alkaline taste and odour, and instantly turns reddened litmus paper blue. In all its chemical relations, it exhibits the closest resemblance to caustic potash. When evaporated in an open vessel, it absorbs carbonic acid, and then effervesces strongly with acids; but on the addition of lime-water, carbonate of calcium is precipitated, and the pure base is again found in the solution. It expels *ammonia* from ammoniacal salts, even in the cold, and separates *baryta* from iodide of barium. *Lime* and *oxide of lead* are immediately precipitated by the solution of this base. With *zinc-salts* it forms a white precipitate, soluble in excess; with *copper-salts* a precipitate insoluble in excess; with *mercurous*, *mercuric*, and *silver-salts*, it gives the same reactions as potash; with *chloride of platinum*, it forms a yellow precipitate, resembling the chloroplatinate of potassium. The aqueous solution, boiled with *sulphur*, forms a yellow liquid, which, when mixed with dilute acids, yields a precipitate of sulphur, and gives off sulphuretted hydrogen.

Iodide of Stibmethylium, $SbMe^4I$, is formed by the action of iodide of methyl on stibtrimethyl. If, in the preparation of stibtrimethyl, the iodide of methyl which distils over at first, and the stibtrimethyl which passes over when the temperature is raised, are collected in the same receiver, a slight ebullition takes place, and the liquid mixture solidifies after a while into a perfectly white, crystalline mass. This is dissolved in warm water, the excess of iodide of methyl separated, and the solution set aside to evaporate slowly over the water-bath. The iodide of stibmethylium then separates in crystals belonging to the hexagonal system. They are remarkably beautiful, large, six-sided tables, usually scalariform, and from 10 to 15 millimetres in diameter; the terminal faces are plane, and the lateral edges intersect one another at angles of 120°. The crystals contain water mechanically enclosed, and consequently decrepitate when heated. They dissolves in 3·3 pts. of water at 23° C., and are likewise easily soluble in alcohol, but dissolve very slowly in ether.—Iodide of stibmethylium heated in a test-tube first falls to powder, and at 200° C. begins to decompose, disappearing gradually, and evolving thick white fumes, which have the odour of stibtrimethyl. The vapour thus evolved is partly deposited as a coating on the inside of the tube; but the greater portion reaches the mouth, where it takes fire spontaneously, forming rings of smoke like phosphoretted hydrogen. Boiling water dissolves but a small portion of the deposit in the tube. The solution treated with *nitrate of silver*, yields a precipitate consisting of iodide of silver and metallic silver, the latter being doubtless produced by pure stibtrimethyl or stibmethylium, the former by undecomposed iodide. The aqueous solution of iodide of stibmethylium is gradually decomposed by repeated *evaporation*, a small quantity of a yellow insoluble substance (not yet examined) being formed, and the odour of stibtrimethyl evolved. The yellow substance likewise appears, though not constantly, when the solution is exposed to sunshine. [For the decomposition by electrolysis, see page 345.] Filtering paper, covered with strong starch-paste, to which iodide of stibmethylium has been added, behaves towards *ozone*, exactly in the same manner as paper prepared with iodide of potassium, but is even more sensitive. *Sulphuric acid*, *bromine*, *chlorine*, and *nitric acid*, act upon iodide of stibmethylium exactly as upon iodide of potassium; *hydrochloric acid* decomposes it, with formation of chloride of stibmethylium. Aqueous solution of iodide of stibmethylium poured upon *amalgam of sodium*, produces a succession of little explosions, accompanied by appearance of fire, metallic antimony being also separated. The iodide distilled with excess of *antimonide of potassium*, yields a yellow oily liquid, which is perhaps stibmethylium. The aqueous solution dissolves a considerable quantity of the yellow modification of *mercuric iodide*. The red iodide boiled in the solution changes into the yellow modification before it dissolves; and as the liquid cools, a considerable portion of the mercuric iodide separates out, but always in the yellow modification.

Nitrate of Stibmethylium, $SbMe^4.NO^3$.—Formed by adding nitrate of silver to an aqueous solution of iodide of stibmethylium as long as any precipitate is formed, then filtering and evaporating till the salt crystallises. The crystals are anhydrous. The salt dissolves readily in water, slowly in alcohol or ether. Its taste is harsh and bitter, not cooling like that of nitre. When heated, it gives off white fumes, which immediately take fire; the entire mass then explodes with a large white flame, just like a mixture of nitre and charcoal. The salt is very stable, not being decomposed, even by boiling with strong sulphuric acid.

Sulphates of Stibmethylium.—The neutral sulphate, $(SbMe^4)^2.SO^4$, is obtained by adding a hot solution of sulphate of silver to aqueous iodide of stibmethylium, as long as any precipitate of iodide of silver is formed. On evaporating the filtered liquid over the water-bath, colourless crystals are obtained, which may be pressed between paper and dried in the air; also, by saturating a concentrated solution of the acid salt with oxide of stibmethylium, and mixing the aqueous solution with alcohol and ether; the neutral salt then separates in oily drops, which after a while assume the solid form. The crystals, which appear to be rhombic, contain 15·42 per cent. (5 at.) water of crystallisation, which they give off at 100° C. Placed over sulphuric acid, they lose part of their water, and fall to a white powder. The crystals dissolve very readily in water; the anhydrous salt becomes strongly heated when water is poured upon it. The salt is also soluble in alcohol, but insoluble in ether. Its taste is saline and bitter.

Acid Sulphate, $(SbMe^4).H.SO^4$.—Obtained by adding 1 at. sulphuric acid to an aqueous solution of 1 at. of the neutral sulphate. After several crystallisations, beautiful, hard, transparent crystals are obtained, some of which are four-sided tablets with obliquely truncated edges. It has a strongly acid taste, leaving a bitter taste in the mouth. When heated, it behaves exactly like the neutral sulphate. On dissolving it in a small quantity of water, then adding alcohol, precipitating by ether, and repeating these operations several times, the neutral sulphate is at length obtained. In this respect, the acid salt behaves exactly like acid sulphate of potassium. The salt contains no water of crystallisation. The basic water (or hydrogen), like that of acid sulphate of potassium, is not driven off at 120° C.

Sulphide, $(SbMe^4)^2S$.—Prepared, like monosulphide of potassium, by dividing an aqueous solution of oxide of stibmethylium into two parts, saturating the one with hydrosulphuric acid, and then adding the other. The resulting solution, quickly evaporated in a retort, leaves the sulphide in the form of an amorphous green powder, which smells like mercaptan, dissolves readily in water and alcohol, but is insoluble in ether. The solutions give black precipitates with lead- and silver-salts. Heated in a tube, it melts and decomposes, giving off spontaneously inflammable vapours, and leaving sulphide of antimony. In contact with the air, it oxidises rapidly.

A solution of hydrate of stibmethylium boiled with sulphur, yields milk of sulphur on the addition of an acid: hence it is probable that higher sulphides of stibmethylium may be formed.

STIBTRIMETHYLETHYLIUM, $Sb(CH^3)^3(C^2H^5)$, is obtained as an iodide by the action of iodide of ethyl on stibtrimethyl. It closely resembles the iodide of stibmethylium.

STIBMETHYLTRIETHYLIUM, $Sb(CH^3)(C^2H^5)^3 = SbMeE^3$. (Friedländer, J. pr. Chem. lxx. 443; Gm. xiii. 500).—The *iodide* of this radicle, obtained by the action of iodide of methyl on stibtriethyl, forms beautiful crystals, apparently having the form of rhombic prisms, with a glassy lustre when fresh, changing after a while to nacreous; they crumble to pieces when dry, but are otherwise permanent in the air. The iodide has an intensely bitter taste, is inodorous when cold, but at 100° C. gives off a peculiar odour, without sensible decomposition. It dissolves in twice its weight of water at 20° C., is soluble also in alcohol, but insoluble in ether. The solutions turns the plane of polarisation to the left.

Iodide of stibmethyltriethylium forms two double salts with *mercuric iodide*, viz. $SbMeE^3I.2HgI$, obtained by adding recently precipitated mercuric iodide to a solution of iodide of stibmethyltriethylium; and $SbMeE^3I.3HgI$, which is precipitated on adding a hot solution of mercuric chloride to a boiling solution of iodide of stibmethyltriethylium, the chloride of the antimony-radicle then remaining in solution:

$$4SbMeE^3I + 3HgCl = SbMeE^3I.3HgI + 3SbMeE^3Cl.$$

This double iodide is insoluble in water, and sparingly soluble in alcohol and ether, crystallising from the alcoholic solution in yellow needles which melt below 100° C.

Chloride, $SbMeE^3Cl$.—Produced as above, or by dissolving the hydrate or carbonate in hydrochloric acid, and may be obtained by evaporation in small crystalline needles.

Hydrate.—Produced (1), by decomposing the iodide with moist oxide of silver (when thus prepared, however, it always contains silver); or (2), by decomposing the sulphate with an exactly equivalent quantity of hydrate of barium, and concentrating the filtrate in vacuo. It is a thick, oily, non-volatile liquid, which has a strong bitter taste and alkaline reaction, decomposes ammonia-salts, and precipitates metallic oxides from their solutions, the zinc and alumina precipitates being soluble in excess.

Hydrate of stibmethyltriethylium dissolves in acids, forming neutral and acid salts, which may likewise be prepared by double decomposition from the iodide, chloride, or sulphate. The salts are more or less soluble in water and alcohol; some are deliquescent, others permanent. Those which crystallise do not contain water. There are no basic salts of stibmethyltriethylium.

The *carbonate*, $(SbMeE^3)^2.CO^3$, is a white resinous mass which reacts like carbonate of ammonium. The *sulphate*, $(SbMeE^3)^2.SO^4$ is produced by dissolving the hydrate in sulphuric acid, or by decomposing the iodide with sulphide of silver, and may be obtained, by evaporation in vacuo, in white, shining, bitter crystals, which melt at 100° C. and are extremely deliquescent.

The *acetate*, *formate*, and *butyrate* are crystalline. The *neutral oxalate*, $(SbMeE^3)^2.C^2O^4$, forms anhydrous glassy needles, moderately soluble in water. The *acid oxalate*, $SbMeE^3.H.C^2O^4$, forms needles very soluble in water. The *tartrate* is obtained by evaporation as a syrupy liquid which rapidly absorbs water, but does not crystallise.

The *cyanide* is obtained by dissolving the hydrate in hydrocyanic acid. The clear watery solution boiled with potash-ley gives off ammonia and forms an antimonetted acid, which yields insoluble or sparingly soluble salts with all bases, except potash, soda, and ammonia.

ANTIPHLOGISTIC THEORY. See Combustion.

ANTIRRHIN. See Anthokirrin.

ANTIRRHINIC ACID. An acid of unknown composition, obtained by Morin from the leaves of the fox-glove (*Digitalis purpurea*). It is prepared by distilling the leaves with water, saturating the distillate with baryta, evaporating, distilling the residue with excess of sulphuric or oxalic acid, and rectifying over chloride of calcium. The acid then floats on the top of the liquid in oily drops, having an unpleasant odour like that of the plant, and producing headache and giddiness. It reddens litmus strongly, dissolves readily in alcohol, and in contact with water forms white films, which gradually dissolve. (J. Pharm. April 1845, p. 299.)

ANTISEPTICS. Substances which prevent the spontaneous decomposition of vegetable and animal substances. They are chiefly: the mineral acids, the alkaline hypochlorites, common salt, nitre, spices, sugar, creosote and yeast. (See Fermentation and Putrefaction.)

ANTITARTARIC ACID, also called *Lævotartaric* and *Lævoracemic* acid. Pasteur has shown that racemic acid, which has no action on polarised light, is a compound of two acids in equal proportions, one of which turns the plane of polarisation of a ray of light to the right, and the other to the left. Hence he calls these acids respectively, *dextro-* and *lævoracemic acids*, or *dextro-* and *lævo-tartaric*. The dextro-acid is identical with ordinary tartaric acid. Gmelin (Handb. x. 365) retains the name *tartaric* for the ordinary dextro-rotatory acid, and distinguishes the lævo-rotating acid as antitartaric acid. (See Tartaric and Racemic Acids.)

ANTRIMOLITE. A hydrated silicate of aluminium, found in white stalactitic masses on the north coast of Antrim. According to Th. Thompson's analysis (J. pr. Chem. viii. 489) it contains 43·47 per cent. of silica, 30·26 alumina, and 15·32 water, together with 7·50 per cent. lime, 4·10 potash, 0·19 protoxide of iron, and 0·098 chlorine. It appears to be related to mestoype.

ANTS, OIL OF. The red ant (*Formica rufa*) contains a volatile oil, which may be extracted by distilling the insects with water: to the amount of 0·12 per cent., according to Nölle; 1 per cent. according to Hermbstadt. It is transparent and colourless, and has an agreeable odour; its taste is not burning. It is slightly soluble in absolute alcohol. (Gm. xiv. 358.)

ANTYRRHINIC ACID. The name given by Walz to a volatile acid, obtained by distilling toad-flax (*Antirrhinum Linaria*, L., *Linaria vulgaris*, Dec.) with water. It forms a deliquescent barium-salt, the analysis of which gives for the atomic weight of the acid the number 212.

ANYLAMIDE. Syn. with Nitrosalicylamide. See Salicylamide.

APATELITE. A native basic sesquisulphate of iron = $2(Fe^4O^3.3SO^3) + 3H^2O$, found, in egg-shaped, earthy, yellow masses, in the clay, at Meudon and Auteuil, near Paris.

APATITE. *Phosphate of calcium.*—This mineral occurs both massive and crystallised. The crystals are six-sided prisms, belonging to the rhombohedral system, sometimes passing into the six-sided table; often hemihedral. Lustre vitreous, inclining to subresinous. Translucent, rarely transparent. Scratches fluor-spar, but is scratched by felspar. Brittle. Colours, white, wine-yellow, green, and red. Specific gravity 3·17 to 3·25. Phosphoresces on coals. Electric by heat and friction. It occurs in primitive rocks; in the tin veins of the granite of St. Michael's Mount, Cornwall; near Chudleigh in Devonshire; at Nantes in France; on the St. Gothard; and with molybdenum in granite, near Colbeck, Cumberland; also at Ehrenfriedersdorf, in Saxony, in the Tyrol, in Bavaria, in Bohemia, and in Spain. Large crystals are found near New York — one crystal from Robinson's farm being nearly a foot in length, and weighing 18 pounds — also in New Hampshire, in Maine, Massachusets, and Delaware. A massive variety called *Phosphorite*, because it becomes phosphorescent by friction, is found in veins of tin-stone, and likewise in secondary formations. A very large vein of this mineral is found at Estremadura in Spain. It has a botryoïdal and kidney-shaped surface, and a radiating fibrous texture.

The chemical composition of apatite may be expressed, according to Gustav Rose (Pogg. Ann. ix. 185), by the general formula, $3PO^4Ca^3 + \begin{matrix} Ca\,F \\ Ca\,Cl \end{matrix}$, the chlorine and fluorine, which are isomorphous, being capable of replacing one another in any proportion whatever. If the chlorine is altogether absent, the mineral becomes a *Fluor-apatite*, or *Francolite*, $3PO^4Ca^3 + CaF$, containing 7·9 per cent. fluoride of calcium, and 92·31 tribasic phosphate. An analysis of Francolite by Dr. Henry gives in 100 pts. 41·34 phosphoric anhydride (P^2O^5), 53·38 lime (Ca^2O), 2·96 protoxide of iron (Fe^2O), 2·32 fluorine, and a trace of chlorine; whence we may calculate that the proportion of tribasic phosphate of calcium is 93·3, and that of the fluoride 4·91; part of the theoretical quantity of calcium is, however, replaced by the iron. The apatites of the St. Gothard, of Ehrenfriedersdorf in Saxony, and of Faldigl and Greiner in the Tyrol, are fluor-apatites. Apatites free from fluorine have not yet been found. The greater number contain chlorine and fluorine together. The largest amount of chloride of calcium is found in the apatite of Snarum in Norway, which contains 4·28 CaCl, 1·59 CaF, and 91·13 PO^4Ca^3. An apatite in which the fluorine was wholly replaced by chlorine would contain 10·62 per cent. of chloride of calcium.

The composition of apatite is only a particular case of the general formula $3\left(\begin{matrix} P \\ As \end{matrix} O^4M^3\right) + \begin{matrix} MCl \\ MF \end{matrix}$ in which M denotes a metal, which, in the species hitherto examined, may be either calcium or lead, and in which phosphorus and arsenic may replace each other in any proportion, as well as chlorine and fluorine. This formula likewise includes the pyromorphites, or green lead-ores, which are isomorphous with apatite. Apatite was so named by Werner from ἀπατεῖν, to deceive, on account of the mistakes of the earlier mineralogists respecting its nature. Even Berzelius was not aware of the presence of phosphorus in it. (Handw. d. Chem. 2^te^ Aufl. ii. 147.)

APATOID. A mineral free from phosphoric acid, found in certain American meteorites.

APELAIC ACID. See Azelaic Acid.

APHANESITE. See Abichite (p. 6).

APHANITE. See Diorite.

APHLOGISTIC LAMP. Lamp without flame, or glow-lamp. (See Alcohol, p. 74.)

APHRITE. *Schieferspar. Chaux carbonatée nacrée.* — A slaty carbonate of calcium, having a mother-of-pearl lustre, found rarely in beds and veins in the older rocks, as in Cornwall, at Kongsberg, &c. A soft friable variety of it, called *earth-foam* (*Schaumkalk*, *Schaumerde*), containing silica and oxide of iron, is found at Gera, and at Eisleben in Thuringia.

APHRIZITE. See Tourmaline.

APHRODITE. A hydrated silicate of magnesium, resembling meerschaum, found at Longbanshytta, in Sweden. Its formula is $16Mg^2O.15SiO^2 + 12H^2O$. Now in the magnesia-silicates, 3 at. water may be supposed to replace 1 at. magnesia (see Silicates) hence the preceding formula may be reduced to $4M^2O.3SiO^2$, or $2MO.SiO^3$ [M denoting a monatomic metal].

APHRONITRUM, (ἄφρος froth and νίτρον soda.) — An old name for the saline efflorescences formed on walls, commonly called *wall-nitre*, but consisting for the most part of carbonate and sulphate of sodium, sometimes with sulphate of magnesium.

APHROSIDERITE. A silicate of iron and aluminium, containing, according to Sandberger, 26·4 per cent. silica, 21·2 alumina, 1·1 magnesia, 44·2 protoxide of iron, and 7·7 water. Sandberger represents it by the formula $3(3FeO.SiO^3) + 3Al^2O^3.SiO^3 + 6HO$. It is doubtful, however, whether all the iron exists as protoxide.

APHTALOSE. See Arcanite.

APHTONITE. The name given by Svanberg to a mineral from Wärmkog, in Wärmeland, resembling fahl-ore (*q. v.*), but distinguished by a peculiarly large amount of basic metallic sulphides. According to Svanberg's analysis (Ofversigt af Kongl.

Vätenskaps Acad. Vörhandlingar, iv. 85), its general formula is $7M^2S.Sb^2S^3$; perhaps a mixture of $6M^2S.Sb^2S^3$ with M^2S. It consists chiefly of copper, zinc, silver, iron, and antimony, with only a trace of arsenic. Specific gravity 4·87.

APIIN.—A gelatinous substance extracted by Braconnot (Ann. Ch. Phys. [3] ix. 250), from common parsley (*Apium petroselinum*) by boiling with water. The boiling liquor passed through a cloth becomes on cooling a transparent jelly, like pectic acid. It is washed in cold water, and after drying over the water-bath, is treated with boiling alcohol and ether, which extract from it a certain quantity of chlorophyll.

Pure apiin is a colourless powder, without odour or taste. It melts at 180°C. into a yellow liquid, which forms a vitreous mass on cooling. It begins to decompose between 200° and 210° C. It is very sparingly soluble in cold water, but dissolves readily in boiling water, which deposits it on cooling in the form of a jelly. It is soluble in boiling alcohol and insoluble in ether. According to Planta and Wallace (Ann. Ch. Pharm. lxxiv. 262) it contains $C^{24}H^{28}O^{13}$. Its solution in boiling water produces a blood-red colour with ferrous salts: this reaction is extremely delicate, sufficing to indicate the smallest traces of apiin. The aqueous solution, after boiling for a long time, no longer gelatinises on cooling, but deposits nearly white flakes, which appear to consist of $C^{24}H^{28}O^{13}.H^2O$. When apiin is boiled with dilute sulphuric or hydrochloric acid, the liquor deposits on cooling, white flakes, which appear to contain $C^{24}H^{20}O^9$, that is to say, apiin *minus* 4 atoms of water. Apiin is dissolved by alkalis and reprecipitated in its original state by acids. When boiled with sulphuric acid and peroxide of manganese, it yields carbonic, acetic, and formic acids.

APIOS TUBEROSA or *Glycine apios* (*L.*)—A leguminous plant from North America, the roots of which have been proposed as a substitute for the potato, and the young seeds for peas. The roots are eaten in Virginia, and are said to have been used by the aborigines of the country. Payen (Compt. rend. xxviii. 189) gives the following statement of the composition of the roots, compared with that of the variety of potato called *patraque jaune:*

	Apios.	Potato.
Nitrogenous matter	4·5	1·7
Fatty matter	0·8	0·1
Starch, sugar, pectin, &c.	33·55	21·2
Cellulose and epidermis	1·3	1·5
Inorganic matter	2·25	1·1
Water	57·8	74·4

APIRIN or **APYRIN.** An alkaline substance said to be contained in the nut of *Cocos nucifera* and *Cocos lapidea*. (Bizio, J. Chim. méd. 1833, 495.)

APJOHNITE. See MANGANESE-ALUM.

APLITE. A name inappropriately given to a kind of granite, consisting chiefly of a fine-ground mixture of quartz and felspar with only a trace of mica.

APLOME. See GARNET.—**APOGLUCIC ACID.** See GLUCIC ACID.

APROCRENIC ACID. See HUMIC ACID.

APOPHYLLIC ACID, $C^8H^7NO^4$.—A nitrogenous acid obtained by the decomposition of cotarnine; first prepared by Wöhler (Ann. Ch. Pharm. i. 24), afterwards more fully examined by Anderson (Edinb. Phil. Trans. xxiii. 347; Chem. Soc. Qu. J. v. 257).

Preparation.—1. Cotarnine is dissolved in nitric acid diluted with twice its volume of water; strong nitric acid is added; and the whole is heated to boiling, whereupon abundance of red vapours are evolved. As soon as a small portion of the solution, on being mixed with alcohol and ether, quickly deposits crystals (if no crystals appear the heating must be continued), the whole of the solution is treated in the same way, and the crystals which are deposited after 24 hours, are filtered off and purified by boiling their solution which animal charcoal, and recrystallising. A great excess of nitric acid hinders the precipitation of the apophyllic acid (Anderson).—2. On decomposing chloroplatinate of cotarnine with sulphuretted hydrogen, filtering off the platinum and evaporating the filtrate with hydrate of barium, apophyllate of barium was found in the residue; and after extracting the cotarnine with alcohol, and boiling the residue with dilute sulphuric acid, a yellow solution was obtained which deposited crystals of apophyllic acid after the lapse of several weeks. (Wöhler.)

Apophyllic acid crystallises from a boiling saturated solution on cooling, in rather long anhydrous prisms, which do not effloresce when heated. It reddens litmus strongly and has a weak acid taste (Wöhler). Melts at 205° C., and solidifies on cooling, into a crystalline mass. (Anderson.)

a. *Hydrated apophyllic acid*, $C^8H^7NO^4 . H^2O$, crystallises from a saturated and not boiling solution, in colourless, very sharp rhombic octahedrons the form of which approaches to that of a square-based octahedron. Angles of the base about 88° and 92°; of the lateral edges, about 106° 28′, 105° 24′, and 190°. The crystals cleave very readily in a direction parallel to the base, forming faces of pearly lustre, like the crystals of apophyllite (hence the name). These give off their water, amounting to about 9 per cent., at a temperature much below 100° C. (Wöhler.)

Aqueous Apophyllic Acid.—Apophyllic acid dissolves slowly and with great difficulty in cold water. It is soluble in sulphuric acid (Anderson); insoluble in alcohol and ether.

When heated, it melts, chars, and evolves an oily, strongly alkaline liquid, which smells like chinoline (Wöhler). By distillation it yields a neutral oil, as well as a base, which does not become coloured when treated with chloride of lime (Anderson).—2. Nitric acid converts it into oxalic acid (Anderson).

Apophyllates.—Nearly all the apophyllates are soluble in water.

Apophyllate of Ammonium forms small prismatic needles. It is readily soluble in water.

Apophyllate of Barium is obtained in nodular crystals by digesting the acid with carbonate of barium and adding alcohol to the solution. (Anderson.)

Apophyllate of Ammonium does not precipitate *lead-salts.* (Wöhler.)

Apophyllate of Silver, $C^8H^6AgNO^4$, is obtained by digesting apophyllic acid with moist carbonate of silver and precipitating the solution with alcohol and ether. It forms a crystalline powder, which burns slowly when heated, leaving a residue of metallic silver. It is easily soluble in water, insoluble in alcohol and ether (Anderson). On mixing a solution of apophyllate of ammonium with nitrate of silver, a double salt, consisting of apophyllate and nitrate of silver, $C^8H^6AgNO^4 . NO^3Ag$, is deposited after a while in small crystalline stars, which soon increase to zeolitic groups of fine needles. The salt explodes violently when heated, like oxalate of silver. It is slightly soluble in water.

APOPHYLLITE. *Ichthyophthalmite, Fish-eye stone.*—A silicate of calcium and potassium, also containing fluorine, which is found both massive and crystallised. The crystals belong to the dimetric system. The most usual form is $\infty P \infty . P$, also with $0P$. Cleavage perfect, parallel to $0P$, imperfect parallel to $\infty P \infty$. The massive variety has a laminated structure. Specific gravity 2·3 to 2·4. Hardness about that of apatite, or generally rather less. The finest varieties are transparent and colourless, or sometimes tinged with rose colour; translucent crystals are also found, or opaque in the mass, translucent only at the edges, and white, reddish-white, or flesh-coloured. External lustre splendent and peculiar; internal lustre glistening and pearly. The transparent crystals exhibit, according to Brewster, a peculiar optical character, which shows that each individual crystal is an aggregate of several pieces symmetrically arranged. In some places (especially at Aussig in Bohemia) a variety called *albin* is found, consisting of opaque crystals of peculiar form. Apophyllite, heated before the blowpipe, exfoliates (hence its name, from ἀποφυλλίζειν), then froths, and melts into an opaque bead. It is easily decomposed by strong hydrochloric acid, with separation of gelatinous silica. The filtrate, supersaturated with ammonia, yields a precipitate of fluoride of calcium.

The composition of apophyllite, as determined by analysis, is as follows:—

	Berzelius.	Stromeyer.	C. Gmelin.
Silica	52·13	51·86	53·90
Potash	5·27	5·31	6·13
Lime (including CaF) . .	25·53	25·22	25·00
Water	16·20	16·91	15·70
	99·13	99·30	100·73

From these results, L. Gmelin (Handb. iii. 394) deduces the formula $KO.2SiO^2 + 6(CaO.2SiO^2) + CaO.SiO^2 + CaF + 16HO$[*], or $15SiO^2.7Ca^2O.K^2O + 2CaF + 16H^2O$.[†] Simpler formulæ may be obtained, if we suppose the fluorine to take the place of part of the oxygen in equivalent proportion. Berzelius gives the formula $KO.2\not{S}iO^2 - 8(CaO.\not{S}iO^2)$[‡] $+ 16HO$, which, if M denote a monatomic radicle, may be reduced to $10\not{S}iO^2.9MO.16HO$. The analytical results may, however, be equally well represented by the general formula $9\not{S}iO^2.8MO.15HO$; and, assuming that $3HO$ may replace $1MO$ (see ISOMORPHISM, POLYMERIC), this formula may be reduced to $9\not{S}iO^2.13MO$,[‡] or $27SiO^2.26M^2O$.

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[*] $Si = 14$; $O = 8$.

[†] $Si = 28$; $O = 16$.

[‡] $\not{S}i = 21{\cdot}5$; $O = 8$.

APORETIN. A resin obtained by dissolving in alcohol that portion of the alcoholic extract of rhubarb which is insoluble in water, precipitating by ether, and again treating the precipitate with alcohol, the aporetin then remaining undissolved (Schlossberger and Döpping, Ann. Ch. Pharm. i. 219). Treated with concentrated nitric acid, it yields a yellow substance, which appears to be chrysammic acid, together with oxalic acid and an acid which produces a brown-red colouring with alkalis. (De la Rue and Müller, Chem. Soc. Qu. J. x. 298.)

APOSEPIDIN. *Käsoxyd.*—A product of the putrefaction of the so-called protein-compounds, discovered by Proust, but since shown by Mulder and others to be merely impure leucine.

APOTHEM. A term applied by Berzelius to the insoluble brown deposit which forms in vegetable extracts when exposed to the air. It is not a definite compound, but a mixture of several substances in a state of decomposition, and therefore of very variable constitution. (See Decay and Putrefaction.)

APPLES. A comparison of various sorts of apples and pears, with regard to specific gravity and amount of water and acid in the juice, has been made by Schulze (J. pr. Chem. lxii. 207). The results vary greatly according to season, climate, and soil; but the general conclusions are as follows:—The specific gravity of the fresh fruit varies from 0·72 to 0·91. The fruits contain between 13 and 21 per cent. of dry substance, of specific gravity above 1·4. The juice of 20 kinds of apples had a specific gravity between 1·020 and 1·027; in two varieties only, it was found to be between 1·033 and 1·037. The acid in the juice, estimated as tartaric acid, amounted to between 0·48 and 1·13 per cent. In Wurtemberg, the specific gravity of the juice of apples and pears rises in warm seasons above 1·080, and even approaches 1·090, the amount of free acid, estimated as tartaric acid, varying from 0·4 to 1·2 per cent., and that of sugar from 4 to 10 per cent.

APPLE-TREE. (*Pyrus Malus.*)—The ash of the branch of an apple-tree contained, after deducting the carbonic acid, in 100 pts.: 19·24 potash; 0·45 soda; 63·60 lime; 7·46 magnesia; 2·41 ferric phosphate; 4·15 phosphoric acid; 0·45 chloride of sodium; 0·93 sulphuric acid; and 1·31 silica. (Fresenius, Handw. d. Chem. 2te Aufl. i. 171.)

APPLE-OIL. *Maloïle.*—A yellowish oil formed in apples when kept. It is lighter than water, has a yellowish-grey colour, a sharp and harsh taste, boils at 190° C., and distils completely; burns with a slightly fuliginous flame; dissolves sparingly in water, but readily in alcohol and ether. Contains 64·15 per cent. carbon, 20·65 hydrogen, and 15·20 oxygen. Forms a crystalline compound with hydrochloric acid, but is decomposed by chlorine. (Handw. d. Chem. 2te Aufl. i. 172.)

APPLE-OIL (ARTIFICIAL). This name is given to a solution of valerate of amyl in 6 or 7 parts of alcohol, which has the smell of apples, and is used as a perfume. (Hofmann, Ann. Ch. Pharm. lxxxi. 87.)

APYRIN. See Apirin.

APYRITE. *Siberite, Rubellite, Red tourmaline.* See Tourmaline.

AQUA FORTIS. This name is given to a weak and impure nitric acid commonly used in the arts. It is distinguished by the terms *double* and *single*, the single having only half the strength of the other. The artists who use these acids call the more concentrated acid, which is much stronger even than the double aqua fortis, *spirit of nitre.* (See Nitric Acid.)

AQUAMARINE. See Beryl.

AQUA-REGIA or **REGIS.** A mixture of nitric and hydrochloric acid, so called from its property of dissolving the noble metals, gold and platinum. (See Nitro-hydrochloric Acid).

AQUA-VITÆ. Ardent spirit of the first distillation has been distinguished by this name in commerce. The distillers of malt and molasses spirits call it *low wines.*

AQUILA ALBA, MITIGATA, CŒLESTIS, MERCURII. An old name for subchloride of mercury; also *mercurius dulcis,* or *mild muriate of mercury.*

ARABIC (GUM). This gum exudes spontaneously from several species of acacia (*Acacia vera, A. arabica*) &c. It was formerly imported into Europe from Egypt and Arabia, but is now obtained chiefly from Senegal. The coarser and cheaper varieties mostly used by calico printers and other manufacturers are known by the name of gum-senegal. (See Gum.)

ARABIN. The principal constituent of gum arabic, in which, according to

Neubauer (Ann. Ch. Pharm. cii. 105), it exists in combination with lime, magnesia and potash. By treating the gum with hydrochloric acid and alcohol, these compounds are decomposed, and the arabin is separated in the form of a gum, which exhibits the properties of an acid. In the moist state, it dissolves readily in cold water, forming a gummy solution, from which it is precipitated by alcohol. After drying at 100° C. it no longer dissolves in cold water, but merely swells up to a gelatinous mass. Dried at 100° C. it has the composition $C^{12}H^{22}O^{11}$, $\frac{1}{11}$ of the hydrogen being replaceable by metals.

ARACHIDIC ACID, $C^{20}H^{40}O^2 = \left.\begin{matrix}C^{20}H^{39}O\\ H\end{matrix}\right\}O$. — Produced by the saponification of oil of earth-nut (*Arachis hypogæa*). The oil is saponified with soda; the mixture of fatty acids separated from the soap by hydrochloric acid, is macerated with five or six times its bulk of cold alcohol to remove the volatile acids; the insoluble portions are pressed and dissolved in alcohol; and the solution, heated nearly to the boiling point, is mixed with such a quantity of acetic acid, that on adding an excess of alcoholic acetate of lead, no precipitation takes place while the liquid remains hot. The crystals which separate after the liquid has remained in the cold for forty-eight hours, are separated from the liquid and mixed with alcohol and hydrochloric acid; the resulting ethers of the fatty acids, after being filtered off from the chloride of lead and freed from part of the alcohol by evaporation, are decomposed by boiling with soda-ley after the alcohol has been completely expelled; the resulting soda-soap is decomposed by hydrochloric acid: and the mixture of fatty acids thus separated, is again dissolved in alcohol, and fractionally precipitated with alcoholic acetate of magnesium. The portions first precipitated contain arachidic acid, which after several crystallisations is obtained pure.

Arachidic acid crystallises in very small shining scales; melts at 75° C., and solidifies again at 73°·5, forming a radiated mass, which after a while assumes the appearance of porcelain. It is but very slightly soluble in cold alcohol of ordinary strength, but dissolves easily in boiling absolute alcohol and in ether. (A. Gössmann, Ann. Ch. Pharm. lxxxix. 1.)

The acid is monobasic, belonging in fact to the series of fatty acids, $C^nH^{2n-1}O^2.H$. The ammonium, potassium, and sodium salts, are soluble in water, the rest insoluble or sparingly soluble in water, but soluble in boiling alcohol. The silver-salt, $C^{20}H^{39}O^2,Ag$, is a white precipitate which separates from boiling alcohol in slightly lustrous prisms, not altered by exposure to light. (Gössmann and Scheven, Ann. Ch. Pharm. xcvii. 257.)

Arachidate of Ethyl, $C^{20}H^{39}O^2,C^2H^5$, obtained by passing hydrochloric acid gas through an alcoholic solution of the acid at 80° or 90° C., is a crystalline, slightly tenacious mass, which melts at 52·5°, and solidifies at 51°. (Gössmann.)

Arachamide, $(C^{20}H^{39}O^2.N^2)N$, is obtained by leaving earth-nut oil for several weeks in contact with ammonia. It forms prisms grouped in stars, insoluble in water, dissolving with tolerable facility in boiling alcohol, melting at 98° or 99° C. When fused with hydrate of potassium, it gives off ammonia.

Arachin, or *Arachidate of Glyceryl*, is obtained by heating equal parts of arachidic acid and syrupy glycerin to 210° C. in a sealed tube. It is a lustrous fatty substance which melts at 70° C., and solidifies in a crystalline mass when slowly cooled. It dissolves sparingly in alcohol of 90 per cent., more freely in absolute alcohol, and still more in ether. It gave by analysis 76·2 per cent. carbon, and 12·6 hydrogen; whereas the formula of *triarachidate of glyceryl*, $C^3H^5O^3.(C^{20}H^{39}O)^3$, requires 77·62 C and 12·6 H (Gössmann and Scheven). Berthelot (Ann. Ch. Phys. [3] xlvii. 355) regards the product obtained by Gössmann and Scheven as a mixture of diarachin with free arachidic acid. He prepares the pure neutral arachins by melting in a flask the crude product obtained by heating glycerin with arachidic acid, then adding slaked lime to neutralise the free acids, digesting with ether for fifteen minutes, and afterwards boiling with ether, which dissolves the neutral fat and leaves the lime-soap undissolved. The ethereal solution when evaporated, leaves the neutral fat, which, if quite free from adhering fatty acids, should form with boiling alcohol a solution which does not redden litmus. In this manner Berthelot has obtained the three neutral arachins, corresponding to the acetins, viz. *monoarachin*, $C^3H^5O^3.C^{20}H^{39}O.H^2$, *diarachin*, $C^3H^5O^3.(C^{20}H^{39}O)^2.H$, and *triarachin*, $C^3H^5O^3.(C^{20}H^{39}O)^3$.

ARACHIS HYPOGÆA. *Earth-nut.* — A leguminous creeping plant, indigenous to India and the coasts of South Africa and South America, and cultivated in North America and in the south of Europe. The flower-bearing stems exhibit, as soon as the fruit begins to form, a tendency to bury themselves in the soil, those which remain above ground bearing little or no fruit. Hence in the cultivation of the plant, the main point to be attended to is to cover up with earth all the flower-bearing stems as soon as the flowers fade. The seeds contain about half their weight of fat oil, *earth-nut oil* (*huile d'arachide, huile de pistache de terre, Erdnuss-öl*), which is extracted from them by pressure. The cold-pressed oil is nearly colourless, has a faint agreeable odour, and may be used for culinary purposes instead of olive oil, only it becomes rancid more quickly. The warm-pressed oil is coloured, and has a disagreeable taste and smell. The cold-pressed oil has a density of 0·916 at 50° C.; and solidifies at − 3° C. When it is exposed for some time to a temperature of + 3°C. a solid fat resembling stearin separates from it. It dissolves but sparingly in alcohol, more readily in ether and essential oils. It saponifies slowly when boiled with caustic soda, yielding a hard, white, odourless soap, which is manufactured in France, and to some extent also in Germany. This soap, when decomposed by the stronger acids, yields two peculiar fat-acids, viz. arachidic acid, $C^{20}H^{40}O^2$, belonging to the series $C^nH^{2n}O^2$, and hypogæic acid, $C^{16}H^{30}O^2$, belonging to the oleic acid series, $C^nH^{2n-2}O^2$ besides a large quantity of palmitic acid. The oil consists therefore of arachin, hypogæin, and palmitin.

ARACHYL. $C^{20}H^{39}O$.—The hypothetical radicle of arachidic acid.

ARÆOMETER. See HYDROMETER.

ARÆOXENE (from ἀραιος, rare and ξένος, guest).—A variety of vanadate of lead, in which a considerable portion of the lead is replaced by zinc, giving the formula $VO^4(Pb;Zn)^3$. Von Kobell found 48·7 per cent. oxide of lead, and 16·3 per cent. oxide of zinc. The mineral, which was formerly mistaken for chromate of lead, is found in clefts of a bed of sandstone, at Dahn in the Rheinpfalz. It forms botryoïdal crystalline masses, exhibiting on the fracture traces of radiating structure. Colour, dark red, inclining to brown; slightly translucent. Streak, light yellow. Hardness 3. Melts quickly before the blowpipe, with intumescence. The powder is easily decomposed by heating with hydrochloric acid. (See Kobell, J. pr. Chem. ii. 496.)

ARBOL-A-BREA RESIN. This resin is the produce of the *Canarium album*, a tree belonging to the natural order *Terebinthaceæ*, which grows in the Phillipine Islands; the resin, which is used by the natives for caulking their canoes, is greyish yellow, soft, glutinous, and has a strong agreeable odour. According to Bonastre (J. Pharm. x. 199) it contains in 100 pts. 61·29 pts. of resin, very soluble in alcohol; 25·00 of resin, sparingly soluble in alcohol; 6·25 essential oil; 0·52 free acid; 0·52 bitter extractive matter; 6·42 woody and earthy impurities. Baup (Ann. Ch. Phys. [3] xxxi. 108) has obtained from it four different crystallisable substances, viz.—

Amyrin.—Insoluble in water, sparingly soluble in cold, easily in hot alcohol, easily also in ether, whence it crystallises in satiny fibres, having a strong lustre. Melts at 174° C. Contains, according to Dumas, 85·3 per cent. carbon and 11·7 hydrogen, and is perhaps identical with crystallised elemi-resin.

Breïdin.—Crystallises in transparent rhomboïdal prisms of 102° and 78°, terminated by four sided pyramids. Dissolves in 260 pts. of water at 10° C. much more abundantly in hot water; easily in alcohol, sparingly in ether,. The crystals become opaque at a gentle heat, melt at a temperature a little above that of boiling water, and sublime undecomposed at a higher temperature, yielding a slightly pungent vapour which excites coughing.

Breïn.—Insoluble in water, soluble in 70 pts. of 85 per cent. alcohol at 20° C.; more soluble in absolute alcohol; very soluble in ether. When slowly crystallised from an alcoholic solution, it forms transparent rhomboïdal prisms of about 70° and 110°, terminated by dihedral summits whose faces meet at about 80°. By rapid cooling acicular crystals are formed. Melts at 187° C. Neutral.

Bryoïdin.—Crystallises from water in white silky filaments. Has a slightly bitter and burning taste, and when heated gives off a vapour which excites coughing. Melts at 135° C., begins to volatilise before melting, and sublimes in colourless needles. Sparingly soluble in cold, much more in hot water, very easily in alcohol and ether. The aqueous solution is neutral to test-paper, but precipitates acetate and subacetate of lead.

ARBOR DIANÆ, ARBOR MARTIS, ARBOR SATURNI, &c. These names are applied to the arborescent metallic precipitates formed by the slow reduction of one metal in solution by another, *e.g.* lead by zinc.

ARBUTIN. A crystalline substance discovered by Kawalier (Ann. Ch. Pharm. lxxxi. 241; lxxxiv. 356) in the leaves of the red bear-berry (*Arctostaphylos Uva Ursi*). The aqueous infusion of the leaves forms with neutral acetate of lead a yellow precipitate containing gallic acid; the filtered liquid freed from excess of lead by hydrosulphuric acid, and then concentrated to the consistence of a syrup, deposits crystals of arbutin, which may be purified by pressure, solution in boiling water, and treatment with animal charcoal. Arbutin forms groups of colourless bitter crystals, which are soluble in water, alcohol, and ether; the solutions are neutral to test-paper.

When heated it melts and gives off water of crytallisation. Its aqueous solution does not form any precipitate with ferric salts, or with acetate or subacetate of lead.

A solution of arbutin mixed with emulsin (extracted from sweet-almonds), and left for some days in a warm place, acquires a reddish tint, and leaves when evaporated over the water-bath, a reddish brown residue, from which ether extracts arctuvin, and leaves a quantity of insoluble saccharine matters. This decomposition of arbutin is represented, according to Kawalier, by the equation:

$$\underset{\text{Arbutin.}}{C^{32}H^{44}O^{19}} = \underset{\text{Arctuvin.}}{C^{20}H^{20}O^{7}} + \underset{\text{Glucose.}}{C^{12}H^{24}O^{12}}$$

but according to Gerhardt, by the equation

$$\underset{\text{Arbutin.}}{C^{18}H^{22}O^{10}} = \underset{\text{Arctuvin.}}{C^{12}H^{10}O^{4}} + \underset{\text{Glucose.}}{C^{6}H^{12}O^{6}}$$

Kawalier's analysis of arbutin gives 52·4 per cent. carbon, and 6·1 hydrogen. His formula requires 52·4 C and 6·0 H; Gerhardt's, 54·2 C and 5·5 H. (Gerhardt, Traité, iv. 266.)

ARCANITE. See GLASERITE.

ARCHIL, ORCHIL, or **ORSEILLE.** A fine purple dye obtained from various species of lichen. There are two varieties, called in France *orseille de mer* and *orseille de terre.* The former is obtained from various lichens of the genus *Rocella* growing on the rocky coasts of the Azores, the Canary and Cape de Verd isles, also of the Cape of Good Hope, Madeira, Corsica, Sardinia, &c.; the latter from *Variolaria orcina*, from Auvergne, *Variolaria dealbata*, from the Pyrenees, *Lecanora tartarea*, from Sweden, and others. None of these lichens contain the colouring matter ready formed, but they contain certain colourless acids, *erythric, lecanoric acid*, &c., which are susceptible of transformation into a colourless neutral body called *orcin* (*q.v.*); and this, when acted upon by the air and by ammonia, changes into a purple substance called *orcein*, which is the colouring principle of archil.

To prepare archil, the lichens, after being ground between stones, are rubbed up to a thin paste with water and putrefied urine or carbonate of ammonium, and left to ferment, with addition of quick lime, a small quantity of alum or arsenious acid being sometimes added, perhaps, to prevent the fermentation from going too far. In a week, a violet colour is obtained, which becomes brighter in a few days longer. When carbonate of potassium or sodium is added to the lichens as well as ammonia, a different change takes place, and a blue colouring matter called *Litmus* is obtained, which is never produced by the action of ammonia alone. (See LITMUS.)

Dyers rarely employ archil by itself, on account of its dearness, and the perishableness of its beauty. The chief use they make of it is for giving a bloom to other colours, as pinks, &c. This is effected by passing the dyed cloth or silk through hot water slightly impregnated with the archil. The bloom thus communicated soon decays upon exposure to the air. The addition of a little solution of tin gives a durable dye, the colour of the archil being at the same time changed toward a scarlet, and becoming more permanent in proportion as it recedes the more from the natural tint.

Prepared archil very readily gives out its colour to water and to alcohol; it is the substance principally made use of for colouring the spirits of thermometers. As exposure to the air destroys its colour upon cloth, so does the exclusion of the air produce a like effect in these hermetically sealed tubes, the spirits of large thermometers becoming in a few years colourless. The Abbé Nollet observes (in the Memoirs of the Académie des Sciences for the year 1742) that the colourless spirit, upon breaking the tube, soon resumes its colour, and this for a number of times successively; that a watery tincture of archil, included in the tubes of thermometers, lost its colour in three days; and that in an open deep vessel it became colourless at the bottom, while the upper retained its colour.

A solution of archil in water, applied on cold marble, stains it of a beautiful violet or purplish-blue colour, far more durable than the colour which it communicates to other bodies. M. du Fay says he has seen pieces of marble stained with it, which in two years had suffered no sensible change. It sinks deep into the marble, sometimes above an inch, and at the same time spreads upon the surface, unless the edges be bounded by wax or some similar substance. It seems to make the marble somewhat more brittle.

There is a considerable consumption of a variety of archil manufactured in Glasgow. It is much esteemed, and sold by the name of *cudbear.* It affords very beautiful colours on silks, of various shades, from pink and crimson to a bright mazarine blue, which are said to be very permanent.—U. (See *Ure's Dictionary of Arts, Manufactures, and Mines*, i. 175.)

ARCTIZITE. See Wernerite.

ARCTOSTAPHYLOS UVA URSI. The *bear-berry.*—An ericaceous plant which grows wild in the mountainous parts of England and Scotland, and in the north of Europe. It possesses strongly astringent properties. The leaves boiled with water yield a liquid which contains tannic acid and a large quantity of gallic acid, and may therefore be used for making ink. The same decoction contains, according to Kawalier, (Ann. Ch. Pharm. lxxx. 356) arbutin, sugar, ericolin, a resinous substance, wax, fat, chlorophyll, vegetable fibre, and a body resembling emulsin, which has the power of inducing the transformation of arbutin. The resin may be separated from the mother-liquor of the preparation of arbutin, by heating it with hydrochloric acid. It is brittle, nearly black, dark brown after trituration, and is said to consist of $C^{20}H^{17}O^{\frac{15}{2}}$, perhaps rather $C^{20}H^{17}O^{8}$. Besides these substances, H. Trommsdorff (Chem. Gaz. 1853, p. 61) also found in the leaves another crystallisable substance which could be extracted by ether, viz. *ursone.*

ARCTUVIN is deposited by evaporating the ethereal solution of the brown residue obtained by the decomposition of arbutin (p. 354), in colourless crystals, which are purified by recrystallisation from water, alcohol, and ether, with the aid of animal charcoal. It forms long prisms, which are bitter, fusible, and may be sublimed when cautiously heated. It contains, according to Kawalier's analysis, 64·4 C and 5·6 H. The formula $C^{20}H^{20}O^{7}$ requires 64·5 C and 5·4 H. Gerhardt's formula, $C^{12}H^{12}O^{4}$, requires 65·4 C and 5·4 H. If sesquichloride of iron be added, drop by drop, to an aqueous solution of arctuvin, the mixture assumes a bluish tint, gradually changing to green. With a solution of subacetate of lead containing a little ammonia, arctuvin forms a white precipitate, which soon turns brown. Arctuvin moistened with ammonia and exposed to the air gradually forms a black substance, which Kawalier calls *arctuvein;* it contains 35·9 C, 3·0 H, 12·5 N, and 48·6 O. (Gerhardt, Traité iv. 266.)

ARECA NUTS, the fruit of the areca palm (*Areca catechu, L.*), contain, as their chief constituents, catechu, a variety of tannic acid, and gallic acid, together with acetate of ammonium, fats, oil, gum, nitrogenous substances, and a dye called *areca-red*, which is of a brown colour, without taste or smell, insoluble in cold water and in ether, soluble in boiling water and alkaline liquids, whence it may be precipitated by acids. Boiled with nitric acid, it yields oxalic acid. (Morin, J. Pharm. viii. 449.)

ARENDALITE. See Epidote.

ARETHASE, a name given by Laurent to a product of the decomposition of chloride of cacodyl by alcoholic potash. (See Arsenic-radicles, Organic.)

ARFWEDSONITE. A ferruginous variety of hornblende. Colour black. Cleavage-faces much more brilliant than those of hornblende, which scratches it. Specific gravity 3·44. Melts even in the flame of a candle; boils up strongly before the blowpipe, and yields a black magnetic globule. Not soluble in acids or in caustic potash. Its composition may be represented by the general formula $Si^{6}M^{10}O^{17} = 5M^{2}O.6SiO^{2}$. A specimen from Greenland, analysed by Kobell (J. pr. Chem. xiii. 3) yielded results agreeing nearly with the formula $(15Fe^{2}O.4Na^{2}O.Ca^{2}O).24SiO^{2}$.

	SiO^2	Fe^2O	Na^2O	Ca^2O	Mg^2O	Mn^2O	Al^4O^3	Cl	
Analysis . .	49·27	36·12	8·00	1·50	0·42	0·62	2·00	0·24	= 98·17.
Calculation . .	52·33	36·93	8·77	1·97	. .	. .	. .	. .	= 100·00.

ARGAL or **ARGOL.** The commercial name of crude tartar in the state in which it is taken from the inside of wine-casks.

ARGENTAN. Syn. of Nickel-silver or German silver. See Nickel.

ARGENTAMMONIUM. A metallic ammonium-radicle (p. 198), containing 1 at. silver in place of hydrogen. Its oxide $(NH^{3}Ag)^{2}O$ is commonly called *fulminating silver.* (See Silver.)

ARGENTINE. A schiefer-spar mixed with silica, found at Southampton and Williamsburgh, in Massachusetts. (See Calcspar.)

ARGENTINE FLOWERS OF ANTIMONY. An old name of tetroxide of antimony, or antimonate of antimony (p. 324).

ARGENTITE or **ARGYROSE.** Syn. of Silver-glance.

ARGILLACEOUS EARTH. See Alumina and Clay.

ARGYRITES. See Lead-oxide. — **ARGYROSE.** See Silver-glance.

ARICINE. $C^{23}H^{26}N^2O^4$ (*Cinchovatine, Cusconine, Quinovine*).—An alkaloid, discovered in white cinchona bark from Arica, by Pelletier and Corriol (J. Pharm. [2] xv. 575). Manzini (J. Pharm. [3] ii. 95) afterwards, found in a fibrous white cinchona from Jaen, an alkaloid which he called *cinchovatine*, but which has been shown by Winckler (Buchner's Répert. d. Pharm. [2] xxxi. 294; xlii. 25 and 231; *ibid.* [3] i. 11) to be identical with aricine.

Aricine is extracted from the cinchona bark in the same manner as quinine (*q. v.*), viz. by boiling the bark with acidulated water, treating the liquor with lime, and digesting the lime-precipitate in alcohol. The solution, filtered at the boiling heat, yields a very dark-coloured liquid, which, after a while, deposits the greater part of the aricine in crystals. An additional quantity may be obtained from the mother-liquor by expelling the alcohol by distillation, treating the residue with a slight excess of hydrochloric acid, separating the greater part of the colouring matter by means of a saturated solution of common salt, then precipitating the aricine by ammonia, dissolving the precipitate in alcohol, decolorising with animal charcoal, and crystallising.

Aricine forms white prismatic crystals, more elongated than those of cinchonine; they are inodorous, and have a bitter taste, which, however, does not show itself for some time, on account of the sparing solubility of the alkaloid. It dissolves easily in alcohol, especially when warm, less readily in ether. The solution blues reddened litmus, and turns syrup of violets green. The crystals, which are anhydrous, melt at 188° C., forming a brownish liquid, which blackens at a higher temperature, yielding fetid empyreumatic products. Aricine dissolves with decomposition in strong nitric acid, forming a deep green solution: this is a very characteristic reaction.

The *salts of aricine* are, for the most part, easily soluble and crystallisable. They are obtained by dissolving aricine in dilute acids; the solutions are precipitated by alkalis. The *acid sulphate*, $C^{23}H^{26}N^2O^4.SO^4H^2$, crystallises in flattened needles (Pelletier), which are anhydrous (Manzini). The *neutral sulphate* does not crystallise from solution in water, but forms a gelatinous mass, which dries up to a horny substance (Pelletier, Ann. Ch. Phys. [2] li. 185). The *platinum-salt*, $C^{23}H^{26}N^2O^4.HCl.PtCl^2$, is soluble in alcohol, and is deposited from the solution by spontaneous evaporation in crystalline plates.

ARISTOLOCHIA CLEMATITIS. *Birthwort.*—The root of this plant, which has a sharp bitter taste, and was formerly much used in medicine, has been examined by several chemists: but the results hitherto obtained are not very definite. When distilled with water, it yields about 0·004 of an essential oil of specific gravity 0·903, and said by Walz to be composed of $C^{11}H^8O^3$. A volatile acid, *aristolochic acid* also passes over, the barium-salt of which contains, according to Walz, $C^9H^6Ba^2O^9$. From the aqueous extract of the root, Walz obtained an impure bitter compound, *clematidine*, $C^9H^5O^6$, which is perhaps identical with the aristolochine obtained by Chevalier from *Aristolochia serpentaria*. Frickinger obtained from the root a bitter uncrystallisable body, and also a yellow crystalline substance, *aristolochia-yellow*, perhaps identical with aristolochine or clematidine. The root also contains a resin soluble in alcohol and ether. The inorganic constituents of the root are: potash 10·3, soda 4·2, chloride of sodium 8·6, lime 9·1, magnesia 3·0, phosphoric acid (PO^5) 14·2, sulphuric acid (SO^3) 1·4, sesquioxide of iron 3·1, silica 4·5, sand, charcoal, and carbonic acid 4·35. (Winckler, Jahrb. pr. Pharm. xix. 71; Frickinger, Buchn. Répert. [3] vii. 1; Walz, Jahrb. pr. Pharm. xxiv. 65; xxvi. 65.)

ARISTOLOCHIA SERPENTARIA. The root of this plant, which had once a great repute in medicine, is now nearly fallen into disuse. Chevalier states that the active principle of it is a yellow bitter substance, which he calls *aristolochine*. The root also contains an essential oil, resins, gum, &c.

ARKANSITE. See Brookite.

ARKI. See Arsa.

ARKOSE. A felspathic sandstone, often having a porphyritic structure, found near Poivin in the Vosges. According to Delesse (Arch. d. Sc. Phys. et Nat. de Genève vii. 177) it has been metamorphosed in the humid way, by taking up the constituents of felspar and hyalite, and gradually transformed into the Vosges sandstone above and granite below.

ARMENIAN STONE. *Lapis Armenius, Armenite.*—An old name for a mixture of earthy azure copper and limestone, sometimes mixed with copper or iron pyrites; or for quartz coloured blue by azure copper.

ARNICA, OIL OF. Both the roots and the flowers of *Arnica montana* contain volatile oils. The oil is obtained from the flowers has a yellow to brownish green colour, dissolves in 100 pts. of alcohol, of specific gravity 0·85, becoming turbid and flocculent, and in 10 to 60 pts. of absolute alcohol, and forms a solid resin when treated with nitric acid. The oil from the roots has a specific gravity of 0·98 to 0·99, and a wine-yellow to brownish yellow colour; dissolves in 2 pts. of alcohol of specific gravity 0·85, and in all proportions of absolute alcohol, and becomes viscid when treated with nitric acid. Both oils have a slight acid reaction. (Zeller, "Studien über ätherische Oele," Landau, 1850.)

ARNICINE. A bitter principle in the flowers of the *Arnica montana.*

ARPIDELITE. See SPHENE.

ARQUERITE. A silver amalgam from the mines of Arqueros in Coquimbo, Chili.

ARRACK. A spirit obtained by fermenting infusion of rice. In Ceylon it is obtained from cocoa-nut toddy (palm wine).

ARRAGONITE. *Rhombic Carbonate of Lime.*—This mineral, which derives its name from the locality where it was first found, viz. in Arragon, occurs sometimes in regular crystals, sometimes in fibrous or radiated crystalline masses, sometimes as a deposit or sinter from hot calcareous springs.

The crystals belong to the trimetric, rhombic, or right prismatic system, and are derived from a right rhombic prism with angles of 116° 16′ and 63° 44′, exhibiting two directions of distinct cleavage parallel to the faces of this prism. Twin-crystals also frequently occur, likewise globular, reniform, and botryoïdal masses, sometimes columnar, composed of straight or divergent fibres.

The crystals of arragonite are seldom colourless, mostly exhibiting a variety of colours; yellowish, greenish, reddish, brown, grey, &c. They have a vitreous lustre, and the powder exhibits phosphorescence on a plate of hot iron. Specific gravity in the pulverulent state, and when free from air, from 2·92 to 3·8; larger masses have occasionally a specific gravity as low as 2·77. Hardness about from 3·5 to 4.

Crystals of arragonite are found in various localities; in clay and gypsum in Arragon; in clefts and cavities of the newer volcanic rocks, especially of basalt, as at Bilin in Bohemia, in Hungary, Scotland, the Feroe Isles, &c.; also in the dolerite on the Kaiserstuhl in the Breisgau; in gneiss and syonite near Dresden and in North America; in the lava of Etna and Vesuvius, &c. *Radiated arragonite*, which forms crude masses having a radiated structure, is found chiefly on the Kaiserstuhl in the Breisgau, at Gergovie in Auvergne, and in Scotland. *Fibrous arragonite, iron-bloom,* or *flos ferri*, occurs in globular, kidney-shaped or stalactitic mass, having a fibrous or laminar texture, and a mother-of-pearl lustre. It is found in veins of iron ore in Carinthia and Styria, Hungary and Transylvania. *Sprudelstein*, a fibrous variety of carbonate of calcium deposited from hot calcareous springs, contains both arragonite and calcspar. *Mountain milk, Rock milk* (*Bergmilch, Chaux carbonatée pulvérulente*), is, according to H. Rose, arragonite mixed with chalk; it occurs in thick, spongy, globular, or kidney-shaped masses, or as a deposit in limestone cavities in Wurtemberg, Switzerland, Bohemia, and other localities. Specific gravity 2·72 to 2·82. It contains traces of organic matter, and leaves a small quantity of charcoal when ignited in a close vessel. *Friable aphrite* (*Schaumkalk, Schaumerde*) was formerly supposed to be a variety of calcspar, but has been shown by Gustav Rose to be arragonite, pseudo-morphosed in the form of gypsum. It occurs sometimes in the form of gypsum-crystals, sometimes as a crystalline or laminar, white or yellowish-white mass. The crystals exhibit a strong nacreous lustre on the cleavage-faces. Its specific gravity, after thorough boiling with water to free it from air, is 2·98. *Alm* or *albene* is a mineral resembling mountain-milk, extensive formations of which are found in Southern Bavaria, where indeed it forms a subsoil many feet in thickness. *Osteocolla* (*Beinbruchstein*) is a carbonate of calcium mixed with sand and organic remains, which collects round decaying roots, and takes their peculiar forms; it is found in the neighbourhood of Berlin. Its specific gravity is 2·82. It exhibits, under the microscope, the form of arragonite mixed with granular masses.

Arragonite consists of carbonate of calcium, CO^3Ca^2, or $CaO.CO^2$, sometimes pure, sometimes mixed with small quantities of the isomorphous compound, carbonate of strontium, which, in the arragonite of Molina, amounts to 4 per cent.; small quantities of the carbonates of magnesium, manganese, iron, &c., are also occasionally found in it. A peculiar variety called *tarnowitzite*, from Tarnowitz in Upper Silesia, contains 3·86 per cent. of carbonate of lead. The chemical properties of arragonite are essentially the same as those of carbonate of calcium in its other forms; dilute acids, however, act upon it less quickly than on calcspar, so that when a mixture of calcspar and arragonite is immersed in a very dilute acid, a residue of arragonite is obtained after a while.

Carbonate of calcium, in its two forms of calcspar (rhombohedral), and arragonite (rhombic or right prismatic), exhibits one of the most striking examples of dimorphism, that is to say, of the same chemical compound crystallising in two forms belonging to different systems (see DIMORPHISM). Formerly, when the existence of dimorphism was unknown, the deviation of arragonite from the more ordinary form of carbonate of calcium was attributed to the presence of carbonate of strontium, which always crystallises in the rhombic system. It was found, however that this mineral was present in arragonite, often in extremely minute quantities, or indeed absent altogether, the form still remaining the same; and thus the fact of the dimorphism of carbonate of calcium became apparent.

Arragonite and calcspar exhibit many differences in their physical properties. Arragonite has two axes of double refraction; calcspar only one. Arragonite has less specific heat (0·1966) than calcspar, greater hardness and greater density. Large crystals of arragonite frequently decrepitate when heated, then swell up suddenly and fall to powder; smaller pieces, or fibrous arragonite, become turbid and rotten. The mineral after this change is found to have the density of calcspar; indeed the change appears to consist in the passage of the arragonite to the form of calspar. This action may explain the pseudomorphoses of calcspar in the form of arragonite. Mitscherlich describes a crystal of arragonite from Vesuvius, which had been converted into calcspar on the outside by the action of the red-hot lava, while its interior still retained the structure of arragonite.

The circumstances which have determined the crystallisation of carbonate of calcium in one form or the other are not precisely known; it appears, however, to assume by preference the form of arragonite, when it crystallises from hot solutions. According to H. Rose (Pogg. Ann. xlii. 363), the precipitate formed on mixing the boiling solutions of chloride of calcium and carbonate of ammonium, consists of microscopic crystals of arragonite, which, however, change into rhombohedrons of calcspar if left for some time under the cold liquid.

The occurrence of arragonite in the deposits of hot calcareous springs points to the same conclusion. The concentration of the liquid appears also to exert some influence. According to Becquerel (Compt. rend. xxxiv. 29 and 573), when gypsum is immersed at ordinary temperatures in a concentrated solution of acid carbonate of sodium, carbonate of calcium is deposited in the form of arragonite, but if the solution of the acid carbonate of sodium is dilute, the deposit takes the form of calcspar. On the whole it would appear that the tendency to the assumption of the arragonite form increases with the rapidity of the crystallisation.

ARROW-ROOT. The starch of the *Maranta arundinacea*, a plant belonging to the order *Marantaceæ*, and cultivated both in the East and West Indies. According to Benzon, the root has the following composition: — Starch 26·00 per cent.; woody fibre 6·00; albumin 1·53; chloride of calcium 0·25; water 65·60 per cent. In the island of St. Vincent, the skinned tubers are washed and ground in a mill, and the pulp is washed in cylinders of tinned copper with perforated bottoms. To obtain the fecula free from impurity, great care must be used in every step of the process. Palette knives of german silver are used for skinning the deposited fecula, and even shovels of the same material for packing it. The drying is effected in pans, covered by white gauze to exclude dust and insects.

The term arrow-root is applied generically to indicate a starch or fecula; thus Portland arrow-root is obtained from *Arum maculatum;* East India arrow-root, from *Curcuma angustifolia;* Brazilian, from *Iatropha manihot;* Tahiti arrow-root, from *Tacca oceanica;* English, from the potato.

Arrow-root, like the rest of the starches, contains $C^{12}H^{20}O^{10}$. The cheaper feculas are sometimes substituted for genuine arrow-root; but they are readily detected by the microscope. Arrow-root is one of the most palateable and digestible of the starches. The expressed juice of the plant has been used as an antidote to poisons and to the bites and stings of venomous insects. (See *Ure's Dictionary of Arts, Manufactures, and Mines*, i. 182.)

ARSA. An alcoholic liquor, procured by the Tartars from fermented mare's milk (Kumis). In the weak state it is called *araca;* after rectification, *arsa.*

ARSENIC. (*Arsen, Scherbenkobalt, Fliegengift, Näpchenkobalt, Arsenicum, Regulus Arsenici*, the ἀρσενικὸν of Dioscorides.) *Symbol*, As. *Atomic weight*, 75. *Vapour-density*, 150 (hydrogen = 1); *Atomic volume*, ½.

History.—This element has been known from very early times, chiefly as sulphide and arsenious acid. The first accurate investigation of its chemical nature was made by Brandt in 1733. Scheele, in 1755, discovered arsenic acid and arsenetted hydrogen gas. Sir H. Davy discovered the solid arsenide of hydrogen. The stoïchiometrical relations of arsenic and its numerous sulphur-compounds, were specially investigated by Berzelius. Bunsen in 1842 discovered cacodyl, an organic radicle containing arsenic and methyl, and several other organic arsenic-radicles have since been discovered by Landolt and others.

Occurrence.—Arsenic is found native, but much more frequently associated with other metals and with sulphur. The ores from which it is prepared on the large scale, as a principal product, in the form of metallic arsenic or arsenious oxide, are: *native arsenic*, As; *arsenical iron*, two species, FeAs, and $Fe^4.As^3$; and arsenical pyrites, $FeAs + FeS^2$. Metallic arsenic and arsenious oxide are likewise obtained as secondary products from *smaltine*, *cloanthite*, *arsenical cobalt*, *cobalt-glance*, *nickel-glance*, *copper-nickel*, *arsenical nickel*, *arsenical fahl-ores*, and other ores of similar character.

These arsenical ores are found more or less abundantly in various parts of the world, but chiefly in the mining districts of Germany and in the Spanish province of Catalonia. In small quantities, arsenic is very widely diffused, being found in the ferruginous deposits of mineral waters (Will, Ann. Ch. Pharm. lxi. 192); in nearly all iron ores (Walchner, *ibid.* 209); in the various kinds of pyrites, and in native sulphur. Hence also it is almost always found in sulphuric acid, and in numerous chemical and pharmaceutical products, in the preparation of which sulphuric acid is used. In short, arsenic in small quantities is one of the most widely diffused substances in nature. It was said by Orfila (J. Chim. méd. xv. 462, 632) to exist also in the bones and muscles of men and animals in a state of health; but the experiments of other chemists have shown this statement to be erroneous.

Preparation.—Metallic arsenic is obtained on the large scale by heating native arsenide of iron, FeAs or Fe^4As^3, or arsenical pyrites, Fe^2AsS, in earthen tubes or retorts: the whole of the arsenic then sublimes, and iron or protosulphide of iron (Fe^2S) remains behind. The retorts are laid horizontally in a long furnace, a tube made by rolling up a piece of thin iron plate, is inserted into their mouths, and an earthen receiver luted on. The arsenic condenses chiefly in the iron tube, in the form of a coherent internally crystalline mass, and when the tube has cooled, is detached by unrolling it. The arsenic thus obtained is purified, if necessary, by a second sublimation. The metal is also prepared by heating arsenious oxide with charcoal in earthen crucibles, surmounted by inverted crucibles, or by conical iron caps. This is the process adopted at Altenberg, in Silesia. It is more productive and economical than the former, but the metal which it yields is grey and pulverulent, whereas the former is compact and nearly white. Arsenic may also be obtained from its sulphides, by heating those compounds with a mixture of charcoal and an alkaline carbonate or cyanide of potassium. (Kerle's Hüttenkunde, iii. 4.)

Properties.—Arsenic is a very brittle metal, of a steel-grey colour. Its specific gravity in the solid state is, according to different observers, between 5·62 and 5·96. Vapour-density = 10·3995 (air = 1), or 150 (hydrogen = 1), which is double the atomic weight; hence the atomic volume of arsenic vapour is anomalous, being only half that of hydrogen. (See ATOMIC VOLUME.) Arsenic crystallises in rhombohedrons, isomorphous with tellurium and antimony. It volatilises at a dull red heat, without previous fusion, emitting a characteristic disagreeable odour resembling that of garlic. Its physical properties vary considerably with the manner in which it is sublimed. When very strongly heated, or when it condenses on a part of the subliming apparatus, the temperature of which is but little below that at which arsenic volatilises, so that the metal is deposited in an atmosphere of its own vapour, it condenses in a compact, nearly white mass, having a strong metallic lustre. This compact arsenic scarcely oxidises in the air, even when pulverised and exposed to a temperature of 80° C. Such is the condition of the metal obtained by heating arsenical pyrites. When, on the contrary, the arsenic, as it passes into the gaseous form, becomes mixed with other gases (as when it is reduced from arsenious acid by charcoal), or when it is deposited on the colder parts of the subliming apparatus, it solidifies in a dark grey crystalline powder, less dense than the preceding, and oxidising readily in the air, especially when heated.

Native arsenic forms botryoïdal, kidney-shaped, spherical, and conchoïdal masses, varying in texture from fine-grained to compact; less frequently, indistinct rhombohedral crystals. In the recent state, it has a light lead-grey colour, but soon becomes greyish-black by exposure to the air. In its chemical properties, it resembles artificially prepared arsenic. It is found in various localities of the Saxon and Bohemian mining districts, at Andreasberg in the Harz, at Kapnik in Transylvania, Kongsberg in Norway, and several places in the United States of America.

Arsenic forms two principal series of compounds, analogous to those of antimony and phosphorus, viz. the arsenious compounds in which it is triatomic, *e.g.* $\overset{'''}{As}H^3$, $\overset{'''}{As}Cl^3$, $(\overset{'''}{As})^2O^3$, $(\overset{'''}{As})^2S^3$, &c., and the arsenic compounds in which it is pentatomic, *e.g.* $(\overset{v}{As})^2O^5$, $(\overset{v}{As})^2S^5$, &c. Besides these, there are a few compounds into which it enters in other proportions, *e.g.* the sulphide AsS, and several alloys.

Many compounds of arsenic are isomorphous with the corresponding compounds of phosphorus and antimony, *e. g. rhombic* arsenious oxide is isomorphous with native trioxide of antimony: the salts of arsenic acid are isomorphous with the corresponding phosphates.

Detection and Estimation of Arsenic.

I. *Reactions in the dry way.*—Metallic arsenic, heated with but slight access of air, as in a narrow test-tube, is converted into a vapour having the peculiar alliaceous odour already mentioned, and condenses on the cold part of the tube in a shining, brownish-black, metallic, ring. With greater access of air, as when a small quantity of the metal is heated in a wide test-tube, or in a tube open at both ends and held over a lamp in a slanting position, the arsenic is converted into arsenious oxide, which condenses on the cold part of the tube in a white crystalline ring, soluble in boiling water.

The oxides of arsenic heated with charcoal or other deoxidising substances, are reduced to the metallic state, the metallic arsenic thus liberated exhibiting the characters just mentioned. If a small quantity of arsenious oxide be placed on charcoal, and the point of the blowpipe flame directed upon it, a greyish-white smoke is immediately evolved, accompanied by a powerful alliaceous odour; and if the arsenious oxide be mixed with perfectly dry and coarsely pounded charcoal, and heated to redness at the bottom of a small test-tube, a ring of metallic arsenic will be deposited on the cold part of the tube.

The sulphides of arsenic, and the salts of arsenious and arsenic acid, are not easily reduced by ignition with charcoal alone, but when heated with carbonate of potassium or sodium, or with a mixture of an alkaline carbonate and charcoal, or cyanide of potassium, they yield metallic arsenic with its characteristic properties.

II. *Reactions in the wet way.* a. Of *Arsenious Compounds.*—*Hydrosulphuric acid gas* passed into an aqueous solution of arsenious acid, colours it yellow, and on addition of hydrochloric acid, throws down the whole of the arsenic in the form of bright yellow trisulphide. The precipitate is said to be perceptible in a solution containing not more than 1 pt. of arsenious acid in 160,000 pts. of water. The precipitate dissolves easily in ammonia, carbonate of ammonium, and sulphide of ammonium, and is reprecipitated without alteration by hydrochloric acid. It is likewise soluble in a considerable quantity of boiling water, and in boiling dilute hydrochloric acid, with liberation of hydrosulphuric acid gas. (Odling, Guy's Hospital Reports [3] i. 239.)

Nitrate of silver added to aqueous arsenious acid produces a scarcely appreciable yellow turbidity, and on cautiously adding ammonia, a canary-yellow precipitate of arsenite of silver, which dissolves with great facility in nitric acid, acetic acid, and excess of ammonia. Hence, if the quantity of arsenic present is but small, it is difficult to avoid adding too much ammonia, and thus preventing altogether the formation of the precipitate. This inconvenience may however be obviated by using a solution of *nitrate of argentammonium*, commonly called *ammonio-nitrate of silver*, prepared by treating a solution of nitrate of silver with a quantity of ammonia sufficient to redissolve only a portion of the precipitated oxide of silver, and filtering. Such a solution contains exactly the proportion of ammonia required to precipitate the arsenious acid as arsenite of silver. If, however, an excess of nitric acid is present, a further quantity of ammonia will be required to neutralise it. In a neutral solution of an arsenite of alkali-metal, nitrate of silver produces an immediate precipitate of arsenite of silver.

With *sulphate of copper*, on addition of ammonia, arsenious acid forms a bright green precipitate of arsenite of copper (Scheele's green), easily soluble in acids and in ammonia. In this case also, it is convenient to use a solution of *sulphate of cuprammonium*, or *ammonio-sulphate of copper*, $SO^4(NH^3Cu)^2$, prepared in the same manner as the ammonio-nitrate of silver.

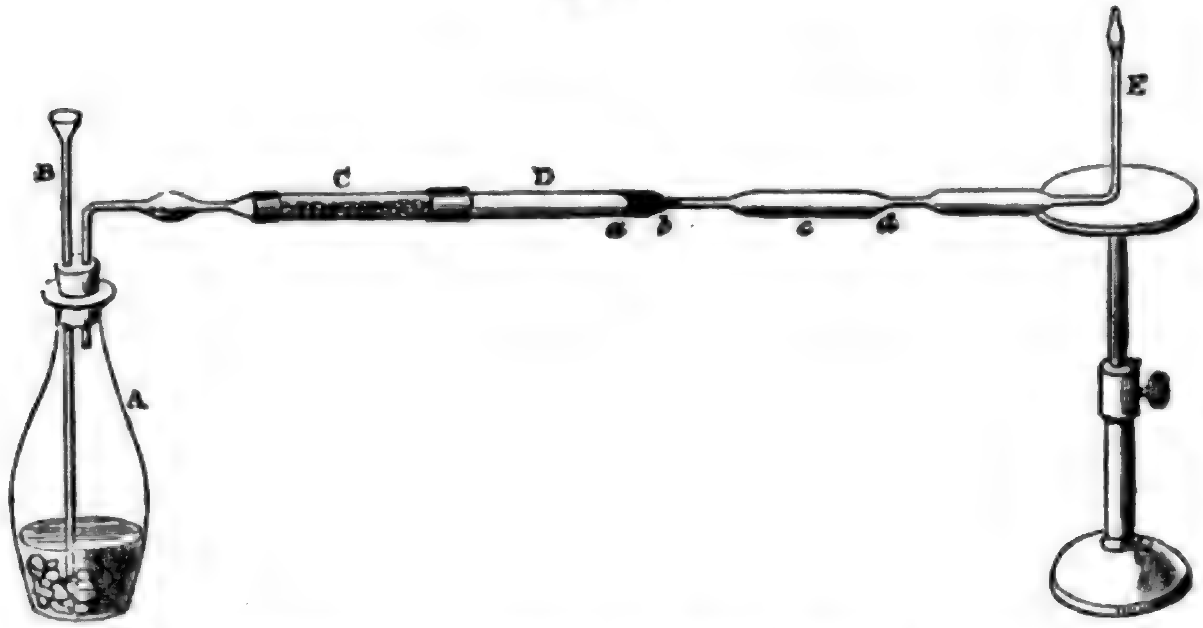
Nitric acid, *hypochlorous* acid, *chromic* acid, and other *oxidising agents*, convert arsenious acid into arsenic acid. With a solution of *trichloride of gold*, it yields arsenic acid, and a black precipitate of metallic gold.

A piece of metallic *copper* immersed in a hot solution of arsenious acid or an arsenite, mixed with hydrochloric acid, becomes covered with a grey film of metallic arsenic, which may be sublimed and converted into arsenious oxide by heating the coated metal in a dry glass tube (Reinsch's test).

Zinc immersed in a solution of arsenious acid or an arsenite acidulated with hydrochloric or sulphuric acid, likewise reduces the arsenic to the metallic state, part of the reduced arsenic being deposited as a black film on the zinc, while the rest unites with the nascent hydrogen and escapes as gas; and from this gas, which burns with a peculiar greyish flame, the arsenic may be separated in the metallic state, either by passing the gas, after drying with chloride of calcium, through a narrow glass tube, one part of which is heated to redness over a lamp, the metal being then deposited in the cold part of the tube beyond the flame; or else by burning the gas at the extremity of the tube drawn out to a fine jet, and holding in the flame, near the orifice, a plate of clean white porcelain. The arsenic is then deposited on the plate in brownish-black, shining metallic films, which may be distinguished from those of antimony formed in like manner (pp. 320, 322), by their solubility in aqueous hypochlorite of sodium, and by other characters to be noticed hereafter.

This reaction, which is known as *Marsh's test*, is extremely delicate, and is therefore much used in searching for minute quantities of arsenic, especially in cases of poisoning. A convenient apparatus for the purpose is that represented in *fig.* 72. A is the generating vessel, provided with a funnel-tube B, for introducing the acid and the solution to be tested. C is a drying-tube containing chloride of calcium; D E the reduction-tube which should be of hard glass, free from lead. It is convenient to have this tube contracted at one or two points, as shown in the figure, and turned up at right angles at the end, so as to form a vertical jet. The first thing to be done is to ascertain whether the zinc and acid are free from arsenic. For this purpose, they must be introduced into the generating vessel, without the solution under examination, and after the evolution of gas has continued long enough to expel atmospheric air, the reduction-tube is to be heated at *a* by a lamp-flame for about a quarter of an hour, and the gas set on fire at the jet E, a piece of white porcelain being held in the flame. If no deposition of arsenic takes place either in the tube or on the porcelain, the liquid to be tested is then to be poured in through the funnel-tube and the heating continued. If arsenic is present, it will be deposited in a shining mirror at *b*, a little beyond the flame. After a sufficient deposit has been obtained at that point, the lamp may be removed to *c*, when a second deposition will take place at *d*, and so on. If the quantity of arsenic is considerable, spots may also be obtained on a plate of porcelain held in the flame at E. The portions of the reduction-tube containing the deposits may then be cut off with a file, sealed, and reserved for further examination. Instead of burning the escaping gas at E, it may be passed, by means of a tube joined to the reduction-tube by a caoutchouc connector, into a solution of nitrate of silver. Metallic silver will then be deposited, and the whole of the arsenic will remain in solution as arsenious acid.

Fig. 72.



A solution of arsenious acid acidulated with hydrochloric or sulphuric acid, is decomposed by the *electric current*, the greater part of the arsenic eliminated at the negative pole being given off in the form of arsenetted hydrogen, which may be examined as above (Bloxam, Chem. Soc. Qu. J. xiii. 14). The apparatus used consists of a two-ounce narrow-mouthed bottle, the bottom of which has been cut off and replaced by a piece of vegetable parchment tightly stretched over it, and secured by a ligature of platinum wire (any ligature of organic nature, even vulcanised caoutchouc, would be quickly destroyed by the ozone evolved at the positive pole). The bottle is furnished with a cork, carrying a small tube bent at right angles, and attached to the reduction-tube by a caoutchouc joint, also a funnel-tube for introducing the liquid to be tested. Through the cork there likewise passes a platinum wire, carrying a plate of the same metal, which forms the negative pole of the voltaic circuit. The bottle is placed within a glass of such a size as to leave a small interval between the two, this glass standing in a vessel of cold water. An ounce of dilute sulphuric acid is introduced into the apparatus, so as to fill the bottle and the outer space to about the same level, the positive plate being immersed in the acid contained in this outer space. The current of a voltaic battery (6 Grove's cells of ordinary size) is then passed through the arrangement, and the shoulder of the reduction-tube is heated to redness for about a quarter of an hour, to ascertain whether any deposit of arsenic is produced from the sulphuric acid itself: if the result be negative, the liquid to be tested is then introduced through the funnel-tube and the heating of the reduction-tube is continued. This method is extremely delicate, even $\frac{1}{1000}$ of a grain of arsenious acid diffused through a considerable quantity of liquid, producing a perceptible deposit in the reduction-tube after 15—30 minutes.

The electrolytic method of eliminating arsenic possesses certain advantages over that of Marsh:—1. It avoids the use of zinc, and thereby obviates a frequent source of error arising from the presence of arsenic in that metal.—2. It introduces no substance into the liquid that can interfere with its subsequent examination for other metals.—3. If any other metals are present, it precipitates them on the surface of the negative plate. Even antimony is for the most part precipitated in this manner. When the reduction is effected by zinc, antimony if present is evolved, together with the arsenic (p. 322), and the subsequent separation of these metals is troublesome; but with the electrolytic method, as above described, only a very small quantity of antimony is evolved as antimonetted hydrogen; and even this quantity may be completely arrested by adding to the liquid a solution of hydrosulphuric acid. Both antimony and arsenic are then converted into sulphides; but the sulphide of arsenic is reduced by the electrolytic hydrogen as easily as arsenious acid (see below), whereas the sulphide of antimony completely resists the action of that agent, and remains in the liquid.

β. Of *Arsenic Compounds.*—A solution of arsenic acid gives with *nitrate of silver*, without addition of ammonia, a red-brown precipitate of arsenate of silver easily soluble in ammonia and in nitric acid. It does not precipitate *sulphate of copper* until ammonia is added, and the precipitate then produced is of a pale bluish-white colour, quite distinct from Scheele's green. With *sulphate of magnesium, ammonia*, and *chloride of ammonium* (the last being added to prevent the precipitation of hydrate of magnesium), arsenic acid forms a white crystalline precipitate of arsenate of magnesium and ammonium, $AsMg^2(NH^4)O^4 + 6H^2O$, similar in appearance and in constitution to the phosphate of magnesium and ammonium. If the solution is very dilute, the precipitate does not appear immediately but is deposited in crystals, after a few hours on the sides of the tube. *Molybdate of ammonium* added in excess to a solution of an arsenate containing free nitric acid, yields, when the liquid is heated, a bright yellow precipitate of arseno-molybdate of ammonium; exactly similar to the phosphomolybdate (see Phosphoric Acid). This precipitate is insoluble in acids, but soluble in ammonia, and in excess of the arsenic solution; hence it is especially adapted for detecting small quantities of arsenic acid, and is indeed one of the most delicate tests for that acid, provided no phosphoric acid is present. With *sesquisalts of iron* and *uranium*, arsenic acid forms yellowish-white precipitates. With *lead-salts*, it forms a white precipitate of arsenate of lead, which when heated on charcoal in the inner blowpipe flame, gives off the odour of arsenic, and yields a button of metallic lead. *Hydrosulphuric acid gas* passed through a solution of arsenic acid colours it yellow at first, and after a long time produces a yellow precipitate of trisulphide of arsenic, mixed with sulphur, the precipitation being accelerated by heat. A solution of a neutral arsenate of alkali-metal, through which hydrosulphuric acid gas is passed, yields the same precipitate on addition of hydrochloric acid. *Sulphurous acid, phosphorous acid*, and other *deoxidising agents* reduce arsenic acid in solution to the state of arsenious acid. Hence in a solution of arsenic acid mixed with sulphurous acid or a soluble acid sulphite, hydrosulphuric acid produces an immediate precipitate of trisulphide of arsenic.

Nascent hydrogen evolved by the action of zinc on dilute sulphuric or hydrochloric acid, converts arsenic acid into arsenetted hydrogen, which is evolved as gas (Scheele, L. Gmelin); but the action is much slower than with arsenious acid. When an *electric current* is passed through a solution of arsenic acid, metallic arsenic is deposited on the negative pole (Gmelin's Handbook, iv.), and arsenetted hydrogen is evolved *provided no chlorides are present* (Bloxam); on adding sulphurous acid, or acid sulphite of sodium to the solution, whereby the arsenic acid is reduced to arsenious acid, the evolution of arsenetted hydrogen is greatly accelerated. The same effect is produced, even with greater certainty on adding aqueous hydrosulphuric acid to the solution. This effect is also chiefly due to the reduction of the arsenic acid to arsenious acid; but even when the hydrosulphuric acid is added in excess, the evolution of the arsenetted hydrogen still takes place, the arsenic uniting with the hydrogen in preference to the sulphur. (Bloxam, Chem. Soc. Qu. J. xiii. 138.)

Compounds insoluble in water, may be examined for arsenic by dissolving them in hydrochloric acid; passing hydrosulphuric acid gas through the solution; digesting the precipitate with sulphide of ammonium, to dissolve out the sulphide of arsenic; and precipitating the sulphide of arsenic by hydrochloric acid. The precipitate may then be dried, and reduced by heating with carbonate of sodium and charcoal, or dissolved in hydrochloric acid, with addition of chlorate of potassium, and the solution, which will contain arsenic acid, tested as above.

The following characters *taken together* are sufficient to distinguish arsenic from all other substances.

1. Formation of a black shining metallic sublimate by one of the methods of reduction above described.

2. Conversion of this metallic deposit into white crystalline arsenious oxide by sublimation in contact with the air.

3. Solution of this sublimate in boiling water, and production of the reactions characteristic of arsenious acid, viz. yellow with hydrosulphuric acid, yellow with ammonio-nitrate of silver, light green with ammonio-sulphate of copper.

4. Solution of the metallic sublimate in hot nitric acid, and production of the reactions characteristic of arsenic acid, viz. red-brown with nitrate of silver, white crystalline with ammonia and magnesium-salts, bright yellow with molybdate of ammonium.

The metal with which arsenic is most likely to be confounded, is antimony, especially when the reduction to the metallic state is effected by Marsh's method, (pp. 320, 322.) The arsenical and antimonial deposits obtained in this manner, may however be distinguished by the following characters:

The arsenic-mirror has a strong lustre, and a black-brown, or brown-black colour; thin films of it formed in a glass tube, appear perfectly translucent, with brown colour, when held before white paper. On account of the volatility of arsenic, the deposit is formed only at a certain distance from the heated portion of the tube, and always on the side *towards* which the stream of gas is directed. The spots formed on porcelain have a black-brown, or when very thin, a brown or light brown colour. The antimony mirror on the contrary is formed in the reduction tube on both sides of the flame and close to it. Where most strongly heated, it has a whiter colour, and when examined by a lens, exhibits small fused metallic globules. It is brownish in thin films, but not continuously brown and shining, like that of arsenic. Antimony-spots formed on porcelain are velvet black, and without lustre, unless very thin; in that case they have an iron-black, or dark plumbago colour, brownish-grey at the edges.

If the part of the reduction-tube containing the arsenic-mirror be cut off, and heated in a *small* lamp flame, the flame exhibits the characteristic greyish colour, and the strong garlic odour of arsenic becomes perceptible. If the pieces of tube covered with arsenic are heated in a narrow test-tube, the characteristic white crystalline sublimate of arsenious oxide is formed, perfectly soluble in boiling water, and exhibiting the characters above-mentioned.

The antimony-deposit does not give off any odour when heated in a lamp-flame, and if heated in a wide test-tube, yields a white shining sublimate of oxide, which is insoluble in water and in ammonia, but dissolves readily in hydrochloric acid, the solution yielding with hydrochloric acid the characteristic red precipitate of antimonious sulphide.

The arsenic-mirror dissolves readily in an alkaline solution *hypochlorite of sodium*, the solution exhibiting the characters of arsenic acid. The antimony-mirror is insoluble in the same liquid, provided it does not contain free chlorine.

Nitric acid of specific gravity 1·2 to 1·3 dissolves the arsenic deposit in the cold, or at a gentle heat, the solution exhibiting the characters of arsenious acid; at a stronger heat, arsenic acid is formed. The same acid likewise dissolves the antimony mirror, but the solution is turbid, gives no precipitate with nitrate of silver and ammonia, orange-yellow, with hydrosulphuric acid.

A very good way to identify arsenic spots is to collect one or more in a watch-glass, add a drop or two of nitro-hydrochloric acid—evaporate quite to dryness, moisten with water, and then add nitrate of silver solution.

Yellow *sulphide of ammonium* dissolves arsenic spots with great difficulty, and never completely; and on evaporating to dryness, there is always left a grey stain of arsenic in the midst of the yellow orpiment. Antimony spots dissolve at once and completely, and the orange-red sulphide of antimony left on evaporation, dissolves completely in hydrochloric acid, being converted into chloride, which volatilises, or leaves only a slight residue of white antimonious oxide.

The arsenic-deposit is easily dissolved in the cold by *hydrochloric acid with addition of chlorate of potassium*, and the solution yields, with magnesium-salts, mixed with ammonia and tartaric acid, the crystalline precipitate characteristic of arsenic acid.

The antimony-deposit similarly treated, dissolves only when heated, and the solution mixed with tartaric acid and ammonia is not precipitated by magnesium-salts.

When arsenetted hydrogen is passed into a solution of *nitrate of silver*, metallic silver is precipitated, and all the arsenic remains in solution as arsenious acid, which may be precipitated by sulphuretted hydrogen, &c.; but when antimonetted hydrogen is passed into nitrate of silver, the whole of the antimony is precipitated in the metallic state, together with the silver, and the solution, after being freed from excess of silver by hydrochloric acid, gives no precipitate with sulphuretted hydrogen.

It often happens that antimony and arsenic are evolved together as gaseous hydrogen-compounds. In that case, the two metals may be separated by the reaction with nitrate of silver just mentioned *; by dissolving the metallic mirror in hydrochloric acid, with addition of chlorate of potassium, then adding tartaric acid and ammonia, and precipitating the arsenic by sulphate of magnesium; or by gently heating the deposit in a very slow stream of dry sulphuretted hydrogen, whereby both are converted into sulphides, and then passing dry hydrochloric acid through the tube. The sulphide of antimony is thereby converted into chloride, which passes on with the stream of gas, and may be received in water and further tested, while the sulphide of arsenic remains unaltered. If the hydrochloric acid gas is not perfectly dry, a small portion of the antimony will be left behind as oxide.

For other methods of separating arsenic and antimony, see page 368.

Detection of Arsenic in cases of Poisoning.—Nearly all compounds of arsenic are poisonous, the most soluble being, generally speaking, those which act with the greatest violence. But arsenious oxide, commonly called *arsenious acid*, being the most generally known and easily procured, is that which is most likely to be met with in cases of poisoning by arsenic, whether accidental or intentional.

As arsenious oxide is but sparingly soluble in water, and is generally administered in the solid state, mixed with viscid articles of food, such as gruel or rice, it sometimes happens that, by careful examination, small lumps of it may be found adhering to culinary vessels, &c., or even to the coatings of the stomach and intestines after death. When this is the case, the arsenic may be picked out and reduced to the metallic state by heating it with charcoal.

If the arsenious oxide is too finely divided to be picked out in this manner, it may sometimes be separated by stirring up the mass several times with water, and leaving the heavier particles to settle. Any solid arsenious acid that may be present will be sure to be found in the residue, and may then be washed with cold water and dried over the water-bath.

The oxide thus separated may be reduced to the metallic state by heating it in a small test-tube with charcoal, as described as page 361. A good way of effecting the reduction, is to place the dried granules or powder at the bottom of a small test-tube, drawn out as shown in *fig.* 73, and place above it a splinter of well-dried charcoal, *a*. The tube is first held in a horizontal position with the part *a* in the flame of a lamp, so as to heat the charcoal to redness; it is then gradually inclined to volatilise the arsenious acid, and cause the vapour to pass over the ignited charcoal. A speculum of metallic arsenic then collects at the shoulder of the tube, and may afterwards be reconverted into arsenious oxide by sublimation in contact with the air, as already described (p. 361).

Fig. 73.

More frequently, however, the arsenic is intimately mixed with large quantities of organic matter, such as articles of food, vomited or evacuated matters, portions of the animal body, as the stomach, liver, &c. In such cases, Reinsch's test (p. 361) may be very conveniently applied. The suspected matter, if liquid, is acidulated with about one-sixth of its bulk of hydrochloric acid and boiled. The solid tissue is cut up into very small pieces and boiled for some time in a mixture of 1 pt. of hydrochloric acid, and 6 parts of water, till the whole is completely disintegrated, and then strained through muslin, or filtered through paper previously wetted. Pieces of copper-gauze or foil are then to be immersed in the boiling liquid, and if any grey deposit is produced, fresh pieces must be added as long as any perceptible alteration of colour takes place on the surface of the metal. They are then to be removed, washed with distilled

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* The best mode of detecting small quantities of antimony thus precipitated is, after carefully washing out the arsenious acid, to digest the precipitate in aqueous tartaric acid; the antimony then alone dissolves, and may be tested by hydrosulphuric acid. (Hofmann, Chem. Soc. Qu. J. xiii. 79.)

water, and dried between bibulous paper, folded up, introduced into a dry test tube, and heated over a lamp. The arsenic is thereby converted into arsenious oxide, which collects on the cold part of the tube in the form of a crystalline sublimate. It may be dissolved in water and tested with nitrate of silver, &c. Inasmuch as Reinsch's process involves the solution of a minute quantity of copper, the foil or gauze employed should be so far free from arsenic that the solution of four or five grains of it should not yield a trace of the poison.

The arsenic may also be detected by other methods which, however, for the most part require more complete destruction of the organic matter. This may be effected by one of the following processes:

1. The organic matter is mixed with about a fourth of its weight of strong sulphuric acid, and heated till the whole is reduced to a dry friable carbonaceous mass; and this residue, after being pulverised, is treated with nitric acid mixed with a small quantity of hydrochloric acid, in order to bring the arsenic to the state of arsenic acid, which is very soluble in water. The mixture is then evaporated to dryness, and the residue boiled with water and filtered. If the organic matter contains alkaline chlorides, which is frequently the case, care must be taken not to heat it more strongly than is necessary for complete incineration, otherwise a portion of the arsenic may be converted into chloride and lost by volatilisation.—2. The organic matter is gently heated in a tubulated retort with strong hydrochloric acid, and nitric acid is added by small portions at a time. The organic matter is thereby completely destroyed, with the exception of the fat. The liquid, which is transparent and colourless, is then decanted from the fatty matters; the latter are well washed with water; and the washings, together with the distillate in the receiver, are added to the main bulk of the liquid (Gaultier de Claubry, J. Pharm. [3] xvii. 125).—3. Chlorate of potassium may also be added in successive portions instead of the nitric acid.—4. The organic matter, after being comminuted as much as possible, may be suspended in water, and chlorine gas passed through the liquid till the organic matter is partly destroyed and partly deposited in brown flakes.—5. The organic matter, after being dried, is mixed with nitre, and the mixture projected by successive portions into a red-hot crucible. The arsenic is thereby converted into arsenate of potassium, which dissolves readily in water. (Wöhler.)

Mr. Graham finds that a most effective separation of the organic matter capable of interfering with the precipitation of arsenic by reagents, may be effected by his apparatus for the diffusion of liquids. A flat hoop of white wood or gutta-percha, about ten inches in diameter, is covered with a sound sheet of parchment-paper, so as to form an instrument like a tambourine in form. The organic fluid is placed within the instrument so as to cover the parchment bottom to the depth of half an inch, and the whole is then floated upon distilled water, contained in a basin. Three-fourths of the arsenious acid present are found to escape by diffusion and enter the water below, in the course of twenty-four hours, giving a perfectly colourless solution. To this liquid, when concentrated, all the ordinary tests of arsenic may be applied. (See DIFFUSION OF LIQUIDS.)

A clear solution having been obtained, the arsenic may be separated from it in either of the following ways:

1. *By Precipitation as Trisulphide.*—The clear arsenical solution is saturated with sulphurous acid to reduce the arsenic acid to arsenious acid, the excess of sulphurous acid is expelled by gentle heating, and a stream of sulphuretted hydrogen gas passed through the liquid for a considerable time. The precipitated trisulphide of arsenic is then carefully washed with cold water, dried, and reduced to the metallic state by heating it in a small tube having a bulb blown at the end with a mixture of dry carbonate of sodium and charcoal, or cyanide of potassium. The bulb, after the introduction of the mixture, should first be gently heated over a lamp to expel moisture, the tube then wiped out with filtering paper, and the bulb strongly heated in the blowpipe flame. A ring of metallic arsenic is then deposited in the tube, and may be treated as already described.

2. *By Conversion into Arsenetted Hydrogen.*—This may be effected either by Marsh's or by Bloxam's process (p. 362). The former has long been used by toxicologists. It is extremely delicate, and indeed has nearly superseded all other methods, excepting that of Reinsch. If the liquid to be tested has been effectually freed from organic matter by either of the methods just given, so that there is no longer any danger of frothing, it may be introduced, together with the zinc and sulphuric acid, into an ordinary gas-generating vessel, provided with a drying tube and reduction-tube (p. 362). Peculiar forms of apparatus have, however, been devised for performing the process without the trouble of completely removing the organic matter. Such is the original apparatus of Marsh, a figure and description of which are given in Graham's Elements of Chemistry, 2nd ed. vol ii. p. 215. Another form of apparatus, contrived for the purpose by a committee of the Prussian government, and

simplified by the late Dr. Ure, is described in *Ure's Dictionary of Arts, Manufactures, and Mines*, new edition, i. 189.

It is found however, that the presence of organic matter sometimes completely prevents the detection of minute quantities of arsenic by Marsh's process (Odling, Guy's Hospital Reports,[3] v. 367; Pharm. J. Trans. [2] i. 374). Hence it is better in all cases, before applying this test, to eliminate the organic matter by one of the processes above described. It must be observed, however, that all these processes yield the arsenic in the form of arsenic acid, so that it becomes necessary to add sulphurous acid or acid sulphite of sodium, in order to reduce it to arsenious acid. Another mode of proceeding, recommended by Odling (*loc. cit.*), is to mix the suspected substance with strong hydrochloric acid, distil to dryness and test the distillate. In this case the addition of sulphurous acid is unnecessary.

Bloxam's electrolytic process is of recent introduction and has not, so far as we are aware, been yet applied in judicial investigations; but it appears to present several advantages over that of Marsh, especially in securing, by the addition of hydrosulphuric acid to the liquid, the complete separation of arsenic and antimony, the former being then evolved as arsenetted hydrogen, the latter remaining wholly in the liquid. The certainty of this separation is of especial importance in the investigation of cases of poisoning by arsenic, inasmuch as tartar-emetic is often given in such cases to produce vomiting.

In all processes of testing for arsenic, it is of the utmost importance to ensure that the indications obtained of the presence of that substance do not proceed from the reagents themselves. Arsenic is very widely diffused in the mineral kingdom, and hence it is by no means an easy matter to procure reagents absolutely free from it. Sulphuric acid, hydrochloric acid, and zinc are often contaminated with it, and consequently Marsh's process, in which these reagents are employed, is very liable to give incorrect indications, unless the precaution be taken of testing the reagents in the manner already described (p. 362) before introducing the suspected liquid. Sulphuretted hydrogen, evolved by the action of dilute sulphuric acid on sulphide of iron often contains arsenic, proceeding from one or both of the substances used; but that which is evolved by heating native sulphide of antimony with hydrochloric acid is generally free from it, because sulphide of arsenic, even if present in the sulphide of antimony, is not decomposed by hydrochloric acid. The complete destruction of organic matter by the processes described at page 366, requires the use of considerable quantities of sulphuric or hydrochloric acid; consequently the arsenic contained in the acid is likely to accumulate in the resulting liquid in sufficient amount to make itself visible in the subsequent examination, even though the proportion of it contained in the acid may be too small to be perceptible in the comparatively small quantities required for the actual testing. This consideration tends rather to induce a preference for methods which do not require so complete a destruction of the organic matters, such as Reinsch's or the electrolytic process.

Quantitative Estimation of Arsenic.—When arsenic is contained in a solution entirely in the form of arsenic acid, it is best to precipitate it in the form of arsenate of magnesium and ammonium, $AsMg^2(NH^4)O^4 + 6H^2O$, by mixing the solution with excess of ammonia, and then with sulphate of magnesium, adding also a quantity of chloride of ammonium sufficient to prevent the precipitation of hydrate of magnesia by ammonia. The liquid is left to stand for some hours, and the precipitate is collected on a weighed filter, and washed with water containing ammonia. It may then be dried, either in vacuo or sulphuric acid, in which case it retains all its water of crystallisation—or more expeditiously at 100 °C., in which case it loses $\frac{11}{12}$ of its water, and is reduced to $AsMg^2(NH^4)O^4 + \frac{1}{2}H^2O$, or rather $2[AsMg^2(NH^4)O^4] + H^2O$, from which the quantity of arsenic is easily calculated.

If arsenic exists in solution in the form of arsenious acid, it may either be brought to the state of arsenic acid by oxidation with nitric acid, and the arsenic determined as above, or the arsenic may be precipitated as trisulphide by hydrosulphuric acid, the solution being previously acidulated with hydrochloric acid, and the precipitate collected on a weighed filter, washed and dried at a temperature a little above 100° C. If the trisulphide were quite pure and definite, its quantity might be at once determined by deducting the weight of the filter from the gross weight, and the quantity of arsenic calculated from the formula As^2S^3. But, as the precipitate almost always contains free sulphur, the quantity of arsenic in it must be estimated by oxidising the sulphur with strong nitric acid, and proceeding in a manner exactly similar to that which has been described for the estimation of antimony (p. 321).

Arsenious acid may also be estimated by its reaction with trichloride of gold, which converts it into arsenic acid, and at the same time yields a precipitate of metallic gold, every 4 at. of gold corresponding to 3 at. arsenious acid:

$$4AuCl^3 + 6H^2O + 3As^2O^3 = 4Au + 12HCl + 3As^2O^5.$$

The gold solution used for the purpose is the sodio-chloride or ammonio-chloride (see Gold): it must be free from nitric acid.

When arsenious and arsenic acids exist together in solution, the latter may be precipitated as ammonio-magnesian arsenate (a considerable quantity of chloride of ammonium being added to prevent the simultaneous precipitation of the arsenious acid); the arsenious acid in the filtrate is converted into arsenic acid by oxidation with chlorate of potassium and hydrochloric acid, and then precipitated in the same manner; or the arsenious acid may be estimated by chloride of gold, as just described.

Atomic Weight of Arsenic.—Berzelius (Schw. J. xxxiii. 172) determined the atomic weight of arsenic from the quantity of sulphurous anhydride produced by heating arsenious oxide with sulphur. The equation, $2As^2O^3 + S^9 = 2As^2S^3 + 3SO^2$, shows that 1 at. As^2O^3, yields $1\frac{1}{2}$ at. SO^2. Now in an experiment made by Berzelius, 2·203 grm. As^2O^3 gave 1·1069 SO^2. Therefore:

$$As^2O^3 = \frac{2{\cdot}201}{1{\cdot}069} \,.\, 96 = 197{\cdot}84$$

and deducting $O^3 = 48$, there results $As^2 = 149{\cdot}84$ and $As = 74{\cdot}92$. Pelouze (Compt. rend. xx. 1014) decomposed pure trichloride of arsenic with water, and determined the quantity of hydrochloric acid produced by means of a standard solution of silver. His results (calculated with the atomic weights of silver and chlorine now adopted ($Ag = 108$; $Cl = 35{\cdot}5$), give as a mean of three experiments, $As = 75{\cdot}08$. The mean between this number and that of Berzelius is exactly 75.

Separation of Arsenic from other Elements.—From other metals of the second and third groups (Analysis, Inorganic), and from all non-metallic elements, excepting selenium, arsenic is separated by precipitation with hydro-sulphuric acid gas in acid solutions. From those metals of the first group whose sulphides are insoluble in alkaline sulphides, *lead*, *copper*, *silver*, &c., it is separated by precipitating with hydrosulphuric acid, digesting the precipitate with sulphide of ammonium, and acidulating the filtered solution with hydrochloric acid. From *selenium* and *tellurium*, it is separated by sulphurous acid, which precipitates those elements from their solutions in the free state.

Separation from Antimony.—When arsenic and antimony exist together in the form of an alloy, they may be completely separated by heating the compound to low redness in a stream of carbonic anhydride, the arsenic then volatilising and the antimony remaining. Antimony is, however, the only metal from which arsenic can be completely separated in this manner; if the alloy contains any other metal, some of the arsenic will be retained, and the method is no longer applicable. When this is the case, the alloy may be dissolved in hydrochloric acid, to which nitric acid or chlorate of potassium is gradually added; the solution diluted with water after addition of tartaric acid, is then mixed with a considerable quantity of chloride of ammonium and excess of ammonia, and the arsenic precipitated by addition of sulphate of magnesium. The antimony may then be precipitated from the filtrate by hydrosulphuric acid. This mode of separation is equally applicable when the two metals are in the state of sulphides; as, for instance, when they are precipitated together from solution by hydrosulphuric acid. When they occur together as oxides, they may be dissolved in hydrochloric acid, mixed with tartaric acid, and treated as above; or they may be separated by fusion with caustic soda in the manner to be presently described.

The separation of arsenic from *tin* may be effected by converting the two metals into sulphides, and separating them, after drying and weighing the whole, by ignition in a stream of hydrosulphuric acid gas. The mixed sulphides are introduced into a weighed glass bulb, having a tube attached to it on each side. One of these tubes, the exit-tube, must be at least a quarter of an inch in diameter, to prevent stoppage, and bent downwards so as to dip into a flask containing ammonia. The whole is then weighed, hydrosulphuric acid gas passed through the apparatus, and the bulb heated till the whole of the sulphide of arsenic is sublimed. Part of the sulphide of arsenic passes into the ammoniacal liquid, by which it is dissolved, and the rest sublimes in the wide tube. When the operation is ended, and the apparatus has cooled, the wide tube is cut off at a short distance from the bulb, then broken, and the pieces digested in caustic potash to dissolve out the sulphide of arsenic. The solution thus obtained is added to the ammoniacal liquid in the flask; the sulphide of arsenic is precipitated by hydrochloric acid, and oxidised, without previous filtration, with hydrochloric acid and chlorate of potash; and the resulting arsenic acid is precipitated by ammonia and sulphate of magnesium. The sulphide of tin remaining in the bulb is converted into stannic oxide by treating it with strong nitric acid.

Separation of Arsenic from Antimony and Tin together.—The separation of these three metals is attended with considerable difficulty. The best mode of effecting it is to convert them into arsenate, antimonate, and stannate of sodium, and treat the mixture with dilute alcohol of a certain strength, which dissolves the arsenate and stannate of sodium, and leaves the antimonate undissolved.

If the three metals exist together in solution, they are precipitated as sulphides by hydrosulphuric acid, and the sulphides are fused in a silver crucible with a mixture of nitre and caustic soda; or, better, they are oxidised by heating them with strong nitric acid; and the solution, together with the insoluble stannic and antimonic acids, is mixed with excess of caustic soda and evaporated to a small bulk, then transferred to a silver crucible, evaporated to dryness, and fused for some time at a red heat. The fused mass, consisting of arsenate, antimonate, and stannate of sodium, is disintegrated by digestion in warm water, the contents of the crucible are transferred to a beaker glass, and the crucible is well rinsed out with a measured quantity of water. The greater part of the arsenate and stannate of sodium then dissolves, while the antimonate remains undissolved. But to effect complete separation, a quantity of alcohol of specific gravity 0·833, is added equal in bulk to one-third of the water used; the mixture is left to stand for 24 hours and frequently stirred; and the antimonate of sodium, which has then completely settled down, is collected on a filter and washed, first with a mixture of 1 vol. of the same alcohol and 3 vols. water; then with 1 vol. alcohol to 2 vols. water; next with a mixture of equal measures of water and alcohol; and, lastly, with 3 vols. alcohol to 1 vol. water.

The antimonate of sodium, separated by this process, is digested in a mixture of hydrochloric and tartaric acids, which dissolves it completely; the antimony is then precipitated by hydrosulphuric acid, and its quantity estimated in the manner already described (p. 320).

The filtrate containing the arsenate and stannate of sodium is supersaturated with hydrochloric acid, which throws down a bulky precipitate of stannic arsenate; hydrosulphuric acid gas is passed through the liquid till the white precipitate is completely converted into a brown mixture of the sulphides of tin and arsenic; the whole is left to stand till the odour of hydrosulphuric acid is no longer perceptible; the precipitate is collected on a weighed filter; and the filtrate is heated for some time to expel the greater part of the alcohol, then mixed with sulphurous acid, and again treated with hydrosulphuric acid, whereby a small quantity of sulphide of arsenic is generally precipitated. This quantity of sulphide of arsenic being quite free from tin, need not be added to the mixed sulphides on the filter. These mixed sulphides are dried at 100° C., their total weight determined, and a known quantity heated in a stream of hydrosulphuric acid gas in the manner described at page 368. The residual sulphide of tin is then converted into stannic oxide, and the sublimed sulphide of arsenic, together with the small quantity separately precipitated, is converted into arsenic acid by treatment with hydrochloric acid and chlorate of potassium, and the arsenic precipitated as ammonio-magnesian arsenate. (H. Rose, Analyt. Chem. 1851, ii. 229.)

This method is long and tedious, but gives accurate results. The most troublesome part of it is the disintegration of the fused mixture of the sodium-salts, which is very hard. To obviate this inconvenience, Professor Williamson dissolves the precipitated sulphides of the three metals in a mixture of sulphide of sodium and caustic soda, and mixes the solution with hypochlorite of sodium. The sulphides are thereby converted into arsenic, antimonic, and stannic acids, which combine with the soda, and may be separated by treatment with dilute alcohol as above.

If the three metals are in the state of solid oxides, the mixture may be dissolved in hydrochloric acid, with addition of tartaric acid, and the metals precipitated as sulphides as before. If the metals are mixed in the form of an alloy, they may be dissolved in aqua-regia, the solution mixed with tartaric acid, then diluted, and precipitated in the same manner.

The method just described may, of course, be applied to the separation of antimony from tin or arsenic alone. In these cases, however, the simpler methods above given are preferable.

Bunsen has lately introduced a new method of separating arsenic from antimony and tin, depending on the action of acid sulphite of potassium on the sulphides of those metals. When recently precipitated trisulphide of arsenic is digested with a solution of sulphite of potassium containing excess of sulphurous acid, it dissolves at first; but on raising the heat to the boiling point, the liquid becomes turbid from deposition of sulphur, which, however, is dissolved for the most part by continued boiling. Sulphurous acid is also given off, and the liquid contains arsenite and hyposulphite of potassium:

$$2As^2S^3 + \underset{\text{Acid sulphite of potassium.}}{16KHSO^3} = \underset{\text{Arsenite of potassium.}}{4KAsO^2} + \underset{\text{Hyposulphite of potassium.}}{6K^2S^2O^3} + 3S + 7SO^2 + 8H^2O$$

The sulphides of tin and antimony are not affected by acid sulphite of potassium. Consequently, when a solution of these three sulphides in sulphide of potassium is precipitated by a large excess of sulphurous acid, the liquid digested for some time over the water-bath, and then boiled to expel the excess of sulphurous acid, the sulphides of tin and antimony remain undissolved, while the whole of the arsenic passes into solution, and may be precipitated from the filtrate by hydrosulphuric acid. If only sulphide of antimony is present in the residue, it may be washed with pure water; but disulphide of tin thus washed is sure to pass through the filter; hence, if tin is also present, the residue must be washed, first with a saturated solution of chloride of sodium, and then with a slightly acid solution of acetate of ammonium to remove the chloride of sodium; after which it may be dried, the ammonium salt then volatilising. The washing cannot be performed with acetate of ammonium alone, because arsenic is never completely precipitated by hydrosulphuric acid from a solution containing acetate of ammonium, that salt being in fact partly decomposed by hydrosulphuric acid into free acetic acid and sulphide of ammonium, which retains the arsenic in solution. Hence the liquid which runs through in washing out the chloride of sodium by acetate of ammonium must not be added to the first wash-water containing the arsenic. (Ann. Ch. Pharm. cvi. 8.)

Valuation of Arsenic Ores. — To ascertain the amount of metallic arsenic that can be obtained from an ore, the ore is gradually heated to redness in a retort or earthen cylinder, either alone or, if it be a sulphide, with potash or quick lime. The greater part of the sublimed arsenic may be collected on a thin iron plate rolled up and inserted into the neck of the retort, and the rest on a cone of copper foil luted on to the neck, a small aperture being left to allow the escape of gases. The sublimed arsenic is then collected and weighed. Commercial arsenious acid may be assayed in a similar manner by heating it with 16 to 20 per cent. of charcoal.

It is seldom required to ascertain the quantity of arsenious acid (anhydrous) that an ore will yield by roasting. A more frequently occurring problem is to determine the proportion of pure anhydrous arsenious acid contained in a crude product. If no other volatile substances are present, the amount of the pure anhydrous acid may be determined by sublimation in a retort; in the contrary case, the arsenious acid may be dissolved out by boiling water, and its amount ascertained by weighing the residue.

The quantity of pure sulphide which may be obtained from an ore, realgar, orpiment, arsenical pyrites, &c., is found by sublimation. (Kerl's *Hüttenkunde*, Bd. iii. 1^te^ Abth. S. 2.)

ARSENIC, ALLOYS OF. *Arsenides.*—Arsenic unites by fusion with most metals, forming alloys which are generally brittle. With *potassium* and *sodium* it forms alloys which give off arsenetted hydrogen gas when thrown into water. With *iron*, *zinc*, and *tin*, it forms brittle compounds; with *copper*, a white malleable alloy; with *gold* and *silver*, grey brittle alloys; with *lead* and with *antimony*, hard, brittle, very fusible compounds. It is introduced into the lead used in the manufacture of shot, to prevent tailing, and cause the metal to run into regular globules.

Metallic arsenides heated out of contact of air, either retain the arsenic altogether or give it up but partially. The alloys of arsenic and antimony are completely decomposed by ignition at a moderate heat in an atmosphere of carbonic anhydride, the arsenic volatilising and the antimony remaining. When an alloy of arsenic is heated in contact with the air, part of the arsenic is evolved as arsenious oxide, while the rest remains in the form of a metallic arsenite or arsenate. The arsenides of the alkali-metals dissolve in hydrochoric or dilute sulphuric acid, with evolution of arsenetted hydrogen; the arsenides of heavy metals are little, if at all, attacked by any acid, except nitric acid or aqua-regia. By fusion with nitre, metallic arsenides are converted into basic arsenates; when the arsenides of the heavy metals are fused with nitre and an alkaline carbonate or hydrate, and the fused mass is treated with water, the whole of the arsenic dissolves as arsenate of alkali-metal, and the heavy metal remains in the form of oxide free from arsenic. Arsenides are not decomposed by fusion with alkaline carbonates alone or mixed with charcoal, but if sulphur be added, a sulpharsenite or sulpharsenate of the alkali-metal is formed, and the other metal remains as sulphide free from arsenic.

Many metallic arsenides are definite compounds in atomic proportion, and in that respect differ from the generality of alloys, which are mere mixtures of their constituent metals in indefinite proportions. In this respect, as in some others, arsenic resembles the metalloïds rather than the true metals. The distinction is, however, not absolute, as many of the metals proper form with one another alloys constituted in definite atomic proportions.

Many metallic arsenides occur as natural minerals, *e.g. copper-nickel*, Ni^2As, *white nickel pyrites*, NiAs, *tesseral pyrites* (Co; Ni; Fe) As, &c.

Arsenide of Antimony, also called *Allemontite*, is found at Allemont, in the Chalanche Mountains, department of Isère; also at Andreasberg, Przibram, &c.; occurring in veins in gneiss, together with native antimony, antimony ores, and arsenical cobalt. It forms fine-grained, spherical, and kidney-shaped masses, with uneven fracture. Specific gravity 6·2. Hardness 3·5. It is of a tin-white colour, opaque, with a faint lustre, and in general appearance more or less resembling native arsenic. It contains, according to Rammelsberg's analysis, 37·9 per cent. Sb to 62·1 As, corresponding to 1 at. Sb : 2·6 at. As [Sb = 120·3], whence it would appear that the two metals are not combined in atomic proportions, but isomorphously mixed.

The other metallic arsenides will be described with the several metals.

ARSENIC, BROMIDE OF, $AsBr^3$, is prepared by shaking arsenic in powder into a retort filled with bromine vapour—the bromide of arsenic being distilled from the excess of arsenic; also, according to Nicklès (Compt. rend xlviii. 837), by treating pulverised arsenic with a solution of bromine in sulphide of carbon: it then crystallises from the solution. It forms a white crystalline mass, which melts at 20°–25° C. to a pale yellow liquid, boils at 22° C., and in the fused state fumes but slightly in the air: in contact with water it is converted partly into arsenious acid and hydrobromic acid, partly into oxybromide of arsenic (p. 385).

ARSENIC, CHLORIDE OF. *Butter of Arsenic; Caustic Oil of Arsenic*, $AsCl^3$.—This is the only known chloride of arsenic, and corresponds to arsenious oxide, As^2O^3. It is produced when finely divided arsenic is brought in contact with chlorine—the metal becoming ignited by the intensity of the combination. The same compound is obtained by distilling a mixture of 1 part of metallic arsenic and 6 pts. of corrosive sublimate; also by distilling arsenious oxide with strong hydrochloric acid, or with common salt and sulphuric acid in excess. A colourless, oily, and very heavy liquid is obtained, which is decomposed by water into arsenious and hydrochloric acid; if the quantity of water is insufficient for complete solution, oxychloride of arsenic (p. 386) is produced. It does not solidify even at −29° C. Boils at 132°, producing a vapour whose density is 6·3006 (Dumas). It evaporates in the air at ordinary temperatures, producing white fumes of arsenious oxide. It is highly poisonous.

Ammonio-chloride of Arsenic, $As^2H^{21}N^7Cl^6 = 2AsCl^3.7NH^3$ (H. Rose, Pogg. Ann. 62 lii.), or $2(NH\overset{'''}{As}.Cl).4NH^4Cl.NH^3$ (Pasteur, Ann. Ch. Pharm. lxviii. 207).—Dry ammonia gas passed into chloride of arsenic is rapidly absorbed, forming a white solid body, which is soluble in water and in alcohol, and crystallises therefrom without alteration. It is decomposed by heat, and according to Pasteur, ammonia is first given off, and then the residue volatilises completely, yielding a sublimate, in which cubes of sal-ammoniac can be detected by the magnifying glass. It is decomposed by hot water, ammonia being evolved, and arsenious acid and sal-ammoniac remaining in solution. When cold water is poured upon it, it becomes heated, gives off ammonia, and forms a solution, yielding by spontaneous evaporation six-sided tables, which may be regarded as a compound of chloride of arsenammonium with arsenious oxide and water, $2(NH\overset{'''}{As}.Cl).As^2O^3.4H^2O$. This compound treated with strong aqueous ammonia is converted into a hard mass of long six-sided tables, consisting of *monammonic arsenite*, $As(NH^4)O^2$, which quickly decomposes in solution, and still more quickly in the solid state, giving off the greater part of its ammonia.

ARSENIC, FLUORIDE OF, AsF^3, is produced by mixing 1 pt. of fluor-spar, purified by ignition, with 1 pt. of arsenious oxide and 3 pts. of strong sulphuric acid in a leaden retort, and heating the mixture till it boils. It is a transparent, colourless liquid, of specific gravity 2·73, very volatile, boiling at 63° C., and fuming strongly in the air even, at ordinary temperatures. The vapour is about four times as heavy as atmospheric air. A drop of the liquid coming in contact with the skin evaporates almost instantly, but nevertheless produces a painful wound, which suppurates for a long time like a burn. It attacks glass but slowly in a close vessel, but in contact with moisture, it is decomposed, yielding arsenious acid and hydrofluoric acid, which corrodes the glass. With water, it forms a clear liquid, which corrodes glass, but scarcely attacks zinc or tin.

ARSENIC, HYDRIDE OF. Arsenic contains two compounds with hydrogen, one solid and the other gaseous. The *solid arsenide of hydrogen* is obtained by passing an electric current through water, the negative pole being formed of metallic arsenic; or by dissolving arsenide of potassium or sodium in water. It is a brown powder, which evolves hydrogen when heated in a close vessel, and burns when heated in the air (Davy). From Soubeiran's analysis, it appears to be AsH^2.

TRIHYDRIDE OF ARSENIC, ARSENETTED HYDROGEN, AsH^3, a gas analogous in composition to ammonia, is obtained:—1. By dissolving arsenide of potassium in water, the solid arsenide being formed at the same time.—2. By dissolving an alloy of 1 at. arsenic and 3 at. zinc or tin, in hydrochloric or dilute sulphuric acid:

$$\mathrm{AsZn^3 + 3ClH = AsH^3 + 3ClZn.}$$

3. By dissolving zinc in hydrochloric or dilute sulphuric acid containing arsenious acid (p. 361.)

$$\mathrm{As^2O^3 + 12Zn} + \left\{\begin{matrix}\mathrm{12Cl} \\ \mathrm{or\ 6SO^4H^2}\end{matrix}\right. \mathrm{= 2AsH^3 + 3H^2O} + \left\{\begin{matrix}\mathrm{12ClZn,} \\ \mathrm{or\ 6SO^4Zn^2.}\end{matrix}\right.$$

4. By dissolving zinc, tin, or iron in aqueous arsenic acid or in a mixture of that acid with hydrochloric or sulphuric acid:

$$\mathrm{2AsH^3O^4 + 16Zn = 2AsH^3 + 8Zn^2O.}$$

This last mode of formation was first given by Scheele, and afterwards denied by Fischer (Pogg. Ann. ix. 261), who stated that aqueous arsenic acid, if quite free from arsenious acid, evolves nothing but hydrogen when treated with zinc. Gmelin, however, obtained arsenetted hydrogen with perfectly pure arsenic acid and zinc. (Handbook, iv. 264.)

5. By the electrolysis of arsenious or arsenic acid. (Bloxam, p. 361.)

The gas obtained by either of the above processes is never pure, but always mixed more or less with free hydrogen. It may be collected over water, but the most scrupulous care must be taken that not the smallest quantity be inhaled, as it is excessively poisonous, and has proved fatal in more than one instance.

Arsenetted hydrogen is a colourless gas, which liquefies at 30° C., but does not solidify even at 110° C. It has an extremely repulsive odour, and even when largely diluted with air, produces nausea, giddiness, and oppression. Small animals are instantly killed by it. It does not redden litmus. Its specific gravity, according to Dumas, is 2·695 (air = 1). One volume of the gas contains $1\frac{1}{2}$ vol. hydrogen and $\frac{1}{4}$ vol. vapour of arsenic: $[\frac{3}{2} \,.\, 0{\cdot}0693 + \frac{1}{4} \,.\, 10{\cdot}39 = 2{\cdot}701]$.

Arsenetted hydrogen is slightly soluble in water. It does not combine either with acids or with bases. It decomposes the solutions of many of the metals which are precipitated by hydrosulphuric acid, its hydrogen alone being oxidised, and the arsenic precipitated in combination with the metal. From a solution of sulphate of copper, for example, it throws down arsenide of copper, $\mathrm{AsCu^3}$:

$$\mathrm{2AsH^3 + 3SO^4Cu^2 = 3SO^4H^2 + 2AsCu^3.}$$

When a mixture of this gas with free hydrogen is placed over a solution of sulphate of copper, the arsenetted hydrogen is completely absorbed and the hydrogen remains. From the salts of silver, gold, and platinum, arsenetted hydrogen precipitates the metals, and is converted into arsenious acid, which remains in solution, *e. g.*:

$$\underset{\text{Nitrate of silver.}}{\mathrm{6NO^3Ag}} + \mathrm{AsH^3 + 3H^2O = 6Ag} + \underset{\text{Nitric acid.}}{\mathrm{6NO^3H}} + \underset{\text{Arsenious acid.}}{\mathrm{AsH^3O.^3}}$$

Arsenetted hydrogen is decomposed at a red heat into free hydrogen and metallic arsenic. It burns in the air with a bluish-white flame, quite different in appearance from that of pure hydrogen, forming water and arsenious acid, which rises in white smoke, and is deposited in a white crust on a cold body, such as a piece of porcelain held just above the flame; but if the porcelain be held in the middle of the flame so as to cool it partially, then the hydrogen is alone burnt, and the arsenic, being less combustible is deposited on the porcelain in metallic spots (p. 362). This effect is precisely similar to the deposition of soot on a glass rod or other cold body held in the flame of a candle.

ARSENIC GLASS. See ARSENIC, SULPHIDES OF (p. 386).

ARSENIC, IODIDE OF. $\mathrm{AsI^3}$.—Arsenic and iodine unite when gently heated together, the combination being attended with considerable evolution of heat. By distilling 3 pts. of iodine with 1 pt. of metallic arsenic, in a retort having its bulb immersed in a sand-bath, the iodide is obtained as an orange-coloured crystalline sublimate having the lustre of gold. It may also be prepared, like the bromide, by treating metallic arsenic with a solution of iodine in sulphide of carbon. It dissolves in 3·32 pts. of boiling water, and the solution, if boiled down, leaves pure iodide of arsenic; but, if left to cool slowly, deposits crystals of a compound of arsenious oxide with oxyiodide of arsenic (p. 368). The iodide may be recrystallised from boiling alcohol, and is then obtained in shining laminæ of a fine brick-red colour. Iodide of arsenic has been used in the treatment of cancer.

ARSENIC, LIVER OF. An old term for the alkaline sulpharsenites (p. 388).

ARSENIC, ORES OF. (pp. 360, 370.)

ARSENIC, OXIDES OF. Arsenic forms two well-defined oxides, viz. the *Trioxide* or *Arsenious Oxide*, As^2O^3, or AsO^3, and the *Pentoxide* or *Arsenic Oxide*, As^2O^5, or AsO^5. The black film which forms on the surface of the metal when exposed to the air is by many supposed to be a suboxide, but it is more probably a mixture of metallic arsenic with the trioxide.

ARSENIOUS OXIDE (or ANHYDRIDE), As^2O^3; in the hydrated state, ARSENIOUS ACID.—This compound occurs native in the mineral *arsenite* or *arsenolite* (*q. v.*) which forms capillary crystals investing ores of nickel, cobalt, &c. It is formed when arsenic volatilises in contact with free oxygen, as when the metal is heated in a glass tube through which a current of air is passing.

On the large scale, arsenious oxide is obtained as an accessory product in the roasting of arsenical ores of tin, cobalt and nickel, and as a principal product in the roasting of arsenical pyrites. The ores are sometimes roasted on the hearth of a reverberatory furnace, where they are in direct contact with the flame, more generally in muffles which are surrounded by the flame but prevent it from touching the material. The latter method involves a larger consumption of fuel, but yields a purer product, inasmuch as when the flame comes in contact with the ore, the arsenious oxide produced by the oxidation becomes mixed with carbonaceous matter, which, in the subsequent sublimation, reduces a portion of the arsenic to the metallic state, and gives the product a grey colour.

At Reichenstein, in Silesia, arsenious oxide is prepared from arsenical pyrites. The ore reduced to powder, is roasted in a muffle-furnace, and the vapour of arsenious oxide is made to pass into a condensing chamber, divided into partitions, where it is deposited in the pulverulent state, as *crude arsenic* or *poison-flour* (*Giftmehl*). This product is refined by sublimation in cast-iron pots, the tops of which are contracted into cones, and terminate in pipes which also pass into a condensing chamber. Lastly, the refined arsenious oxide is again sublimed at a higher temperature, and collects in the upper part of the subliming vessel in the form of a glass (vitreous arsenious oxide).

At Ribas, in Catalonia, arsenious oxide is obtained from arsenical pyrites by roasting in a reverberatory furnace without muffles; in other respects, the series of operations is similar to that just described. At Andreasberg, in the upper Harz, argentiferous native arsenic is roasted to extract the silver, and arsenious oxide is obtained as a secondary product. It is also produced in large quantity in the roasting of tin ores and cobalt ores at Altenberg in Saxony, and of tin ores in Cornwall. (See *Ure's Dictionary of Arts, Manufactures, and Mines*, i. 185; Kerl's *Hüttenkunde*, iii. 1^{te} Abtheilung, S. 14.)

Properties.—Arsenious oxide is a white solid, which occurs in two crystalline forms and likewise in the amorphous state.—1. *Amorphous, vitreous* or *glassy* arsenious oxide is produced, when the vapour condenses on a surface whose temperature is but little below the volatilising point of the oxide, so that before solidifying it passes through the semi-fluid state. It is transparent when first prepared, but gradually becomes opaque, and passes into the crystalline state. Its specific gravity, according to Guibourt, is 3·7385.—2. *Octahedral arsenious oxide.* This variety is produced by sublimation when the vapour is cooled so quickly that it solidifies at once, without passing through the semi-fluid state. A hot saturated aqueous solution deposits the oxide in regular octahedrons on cooling. Vitreous arsenious oxide is transformed into the octahedral variety by keeping, especially in contact with the air, and also by solution in water or hydrochloric acid. When 2 or 3 pts. of the vitreous oxide are dissolved in a mixture of 12 pts. of fuming hydrochloric acid and 4 pts. of water, and the solution is left to cool slowly, the arsenious oxide crystallises in transparent octahedrons, the formation of each crystal being accompanied by a flash of light (H. Rose). The specific gravity of octahedral arsenious oxide is 2·695 (Guibourt).—3. *Right Rhombic Arsenious Oxide.* This variety, which is isomorphous with native oxide of antimony, is occasionally obtained by sublimation (Wöhler), also, according to Pasteur, when a boiling solution of potash is saturated with arsenious acid and left to cool. It is converted into the octahedral variety by sublimation or by solution in hot water.

Arsenious oxide volatilises at about 218° C., forming a colourless vapour of specific gravity 13·85. The vapour is perfectly inodorous, provided the oxide has not been heated in contact with charcoal or other reducing agent. The vitreous oxide may be fused before it volatilises to any considerable extent; but the crystallised oxide sublimes before fusion. Under pressure, the oxide may be melted to a glass.

Arsenious oxide dissolves but sparingly in cold *water*, more readily in boiling water, the vitreous oxide dissolves more readily than the crystalline variety. A hot saturated solution contains 1 pt. of the oxide or anhydrous acid in 10 or 12 pts. of water, and on cooling deposits the greater portion, leaving a solution containing 1 pt. of the anhydrous acid in 30 pts. of water. The statements of different authors regarding the solubility of arsenious acid in water differ considerably, the discrepancy probably arising from the simultaneous occurrence of the vitreous and crystalline modification in the acid submitted to experiment (Gm. iv. 257). No definite hydrate of arsenious acid appears to exist. The aqueous solution is transparent and colourless, and slightly reddens litmus. (For its behaviour with hydrosulphuric acid, nitrate of silver, and other reagents, see page 361.)

Arsenious oxide dissolves in hot *dilute acids* more readily than in water, but separates out completely on cooling, without forming any definite compound. It has therefore little or no basic power. With *tartaric acid*, however, it forms a potassic double salt analogous to tartar-emetic. (See TARTARIC ACID.)

It dissolves in *alkalis*, forming arsenites of alkali-metals.

It is nearly insoluble in *alcohol*, quite insoluble in *ether*.

Arsenious oxide, whether in the dry state or in solution, is one of the most violent of the acrid poisons, a dose of two or three grains being certain to cause death, unless it be very speedily ejected by vomiting, or rendered innocuous by conversion into an insoluble compound. Nevertheless it appears to be possible, by commencing with small doses and gradually increasing them, to accustom the human body to sustain without injury, doses of 4 grains or even more; and it is moreover stated, apparently on good authority, that arsenic thus taken produces a plump and healthy appearance in those who use it, and especially increases the power of the respiratory organs, and consequently facilitates mountain-climbing under heavy burthens. The Tyrolese peasantry are said to swallow arsenic in considerable quantities for this purpose. Those who are accustomed to taking arsenic in this way, are also said to experience great depression and loss of strength if they discontinue it.

Arsenious acid in small doses is much used in medicine, chiefly in cases of skin-disease. The form in which it is most frequently administered is that of *Fowler's solution*, which is an arsenite of potassium.

The best antidote to poisoning by arsenic is *hydrated sesquioxide of iron*, which, when administered in excess, converts the arsenious acid into a basic ferric arsenite, perfectly insoluble in water and in the fluids of the alimentary canal. It may be prepared by precipitating a solution of ferric chloride or sulphate with ammonia, and washing by decantation, and should then be kept under water, because when dry, its power to lay hold of arsenious acid is very much diminished. It is most efficacious when recently precipitated, the absorbing power being somewhat diminished, even by keeping under water (Bunsen and Berthold, "Das Eisenoxyd ein Gegengift der arsenigen Säure." Göttingen, 1834). Still more efficacious, according to Fuchs, is a mixture of hydrated ferric oxide with magnesia, obtained by precipitating a solution of ferric chloride or sulphate with excess of calcined magnesia. It should be prepared at the time when it is wanted, and may be used at once, without washing, the soluble magnesium-salt produced by the reaction being rather beneficial than otherwise, inasmuch as it exerts a purgative action. When ammonia is used as the precipitant, the washing cannot be dispensed with, because arsenite of iron is somewhat soluble in ammoniacal salts. The magnesia used for precipitating the ferric hydrate must not be very strongly calcined. Magnesia itself is likewise capable of abstracting arsenious acid from solution, and forming an insoluble compound with it; but ferric hydrate is more powerful in this respect, and the mixture of the two prepared in the manner just mentioned, is more efficacious than either, probably because the ferric hydrate is spread over the surface of the particles of magnesia in a state of fine division. (Handw. d. Chim. 2te Aufl. ii. 294.)

Arsenious oxide acts both as an oxidising and as a reducing agent. It partially deoxidises many compounds rich in oxygen, *e.g. nitric acid, manganic acid, chromic acid, hypochlorous acid*, &c., being itself converted into arsenic oxide or acid. It quickly reduces *gold* from the solution of the trichloride. *Potassium, charcoal, sodium, sulphur, phosphorus*, and *zinc* deoxidise it at a red heat, separating metallic arsenic. Distilled with *acetates*, it yields cacodyl, a compound of 1 at. arsenic with 2 at. methyl, $As(CH^3)^2$, which may be recognised by its peculiar and intolerable odour. When vapour of arsenious oxide is passed over red-hot *lime*, part off it is resolved into metallic arsenic, which sublimes, and arsenic oxide which unites with the lime, forming an arsenate (Wollaston), while another portion, greater as the heat is less, unites directly with the lime, forming an arsenite (Simon). Heated with *carbonate of potassium*, it likewise yields metallic arsenic and an arsenate (Gay-Lussac). As an oxidising agent, arsenic oxide is used in the manufacture of glass, for the purpose of converting protoxide of iron into sesquioxide, which yields less highly coloured glasses than the protoxide.

ARSENITES.—Arsenious acid unites with bases in several proportions, but the salts are not very stable, and have been but little examined. Those whose composition is $MAsO^2$ or $M^2O.As^2O^3$, are generally regarded as neutral; and besides these there are basic arsenites containing $M^4As^2O^5$, or $2M^2O.As^2O^3$, and M^3AsO^3, or $3M^2O.As^2O^3$, besides acid salts.* Arsenious oxide dissolves in caustic *potash* or *soda*, but does not neutralise the alkali; the concentrated solutions are decomposed by the carbonic acid in the air, and yield, after a while, very large and well formed crystals of anhydrous arsenious acid. The acid dissolves in *ammonia* more readily than in water, and remains free from ammonia when the solution is evaporated. *Lime*, *baryta*, and *strontia*, dissolve when boiled with water and excess of arsenious acid, and on adding lime-, baryta-, or strontia-water in excess to the solutions, basic salts are precipitated in white flocks. These precipitates dissolve in acids and in ammoniacal salts: hence arsenious acid cannot be precipitated by the alkaline earths from solutions containing ammoniacal salts. The other arsenites are insoluble in water, and are obtained by precipitation. They dissolve in hydrochloric acid, and some of them in acetic acid, also in sulphate, hydrochlorate, and nitrate of ammonium.

Solutions of the alkaline arsenites give a light green precipitate with *cupric salts*, egg-yellow with *nitrate of silver*.—*Hydrosulphuric acid* produces no precipitate unless a stronger acid is present in excess; but all arsenites when dissolved in hydrochloric acid give a precipitate with hydrosulphuric acid; and if the metallic base of the arsenite is likewise precipitable by hydrosulphuric acid, a compound metallic sulphide may be produced.

Most arsenites are decomposed by *heat:* some give off arsenious oxide, and leave the base in the form of oxide: but the arsenites of the alkali-metals and the alkaline earth-metals, give off metallic arsenic and leave a salt of arsenic acid ($5As^2O^3 = 3As^2O^5 + As^2$). Arsenite of silver gives off arsenious oxide and leaves a mixture of metallic silver and arsenate of silver; arsenite of lead alone withstands a red heat without decomposition, and arsenite of magnesium is but imperfectly decomposed (Simon, Pogg. Ann. xi. 435).—Arsenites heated with *charcoal* give off metallic arsenic.

Arsenite of Ammonium, NH^4AsO^2, or $(NH^4)^2O.As^2O^3$, according to Pasteur; $(NH^4)^4As^2O^5$, or $2(NH^4)^2O.As^2O^3$, according to Stein, is produced, according to Pasteur, when very strong aqueous ammonia is poured upon arsenious oxide, and forms a hard mass composed of microscopic six-sided tables belonging to the trimetric system. It exists only in contact with ammonia, quickly giving off ammonia in contact with the air. It forms a yellow precipitate with silver-salts, the solution turning acid. It is insoluble in alcohol and in ether.

Arsenite of Antimony.—Produced by digesting metallic antimony with aqueous arsenic acid, and is precipitated on diluting with water. It may also be obtained as a transparent, fused, vitreous mass, by heating metallic arsenic with antimonic oxide.

Arsenite of Barium, $BaAsO^2$, or $Ba^2O.As^2O^3$, is obtained by mixing a solution of chloride of barium with acid arsenite of potassium, separating after a few hours as a gelatinous mass or in dendritic ramifications. In this state it is very soluble in water, but becomes sparingly soluble after drying: the liquid decanted from the jelly likewise yields the salt by evaporation, as a heavy sparingly soluble powder. The gelatinous salt is probably a hydrate. A salt containing $2Ba^2O.As^2O^3 + 4H^2O$ is obtained, according to Stein, by dropping baryta-water into aqueous arsenious acid, as long as a precipitate continues to form, and washing with dilute alcohol. It gives off 2 at. water at 100° C., and the rest at a higher temperature, arsenic, however, volatilising at the same time.

A concentrated solution of arsenious acid is immediately precipitated by baryta-water, a very dilute solution after some time only, or not at all (L. Gmelin). Arsenite of ammonium precipitates solution of chloride of barium after a while.

Arsenite of Calcium.—The several arsenites of potassium, added to solution of chloride of calcium, yield precipitates, but not of constant composition (Filhol). The neutral salt, $CaAsO^2$, is obtained, according to Simon, by precipitating chloride of calcium with ammonia saturated with arsenious acid; the precipitate is increased by adding excess of ammonia, but dissolves partially when washed with water. When, on the other hand, an aqueous solution of arsenious acid is mixed with excess of lime-water, a white heavy powder ($2Ca^2O.As^2O^3$, with water) is precipitated, which is very little soluble in water, somewhat more soluble in the presence of ammonia-salts, or of chloride of potassium or sodium. According to Stein, the precipitate thus obtained is a mixture of several basic salts, but on adding sufficient arsenious acid to dissolve part of it, the residue consists of $3Ca^2O.2As^2O^3 + 3H^2O$; this salt gives off 1 at. water at 100° C., the rest at a temperature at which decomposition begins.

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* If $O = 8$, the formulæ are $MO\ AsO^3$, $2MO.AsO^3$, and $3MO.AsO^3$ respectively.

According to Kühn (Jahresb. f. Chem. 1852, 379), a boiling solution of arsenious acid added to excess of lime-water throws down the salt, $3Ca^2O.As^2O^3$, or Ca^3AsO^3.

Arsenite of Cobalt, $3Co^2O.2As^2O^3 + 4H^2O$, is obtained by quickly mixing arsenite of potassium with a solution of chloride of cobalt containing a large excess of sal-ammoniac.

Arsenite of Copper, $Cu^4As^2O^5$, or $2Cu^2O.As^2O^3$, is obtained by precipitating a salt of copper with arsenite of potassium, or with arsenious acid and a sufficient quantity of ammonia to neutralise the acid present (p. 361). It is a light green precipitate (Scheele's green), which dissolves in excess of ammonia without colour, yielding a solution of arsenic acid and cuprous oxide. Arsenite of potassium containing excess of alkali dissolves it readily, with blue colour, but the solution quickly decomposes into arsenate of potassium and cuprous oxide. Vapour of arsenious oxide passed over red-hot cupric oxide does not combine with it.

Aceto-Arsenite of Copper. $3CuAsO^2.C^2H^3CuO^2$. *Schweinfurt Green*, or *Imperial Green*. —This compound, the preparation of which is given at page 15, is much used as a pigment, on account of its splendid green colour. A great deal of needless alarm has lately been excited about the supposed deleterious effects of this pigment. It is extensively employed for staining wall-papers, and persons inhabiting rooms thus papered are said to have had their health seriously deranged by the *arsenical fumes* evolved from it! Now it is utterly impossible that arsenic should volatilise from such a compound at ordinary temperatures: it does not decompose at any temperature below redness. The only way in which danger could arise from the use of paper stained with an arsenical colour, is that particles of the compound might be brushed off in in dusting the paper, and thus become mixed with the air of the apartment; but it is not in this way that the supposed accidents are said to have occurred; the panic has arisen from a mistaken notion as to the volatility of the arsenic. That the use of the pigment is not really dangerous may be safely inferred from the fact that no bad effects are experienced by the workmen engaged in its manufacture. (See *Ure's Dictionary of Arts, Manufactures, and Mines*, i. 157.)

Arsenite of copper forms a similar double salt with *butyrate* of copper.

Arsenites of Iron.—There are several basic *ferric arsenites*. When recently precipitated ferric hydrate is digested with a concentrated solution of arsenious acid, in such proportion that the quantity of anhydrous ferric oxide present is equal to ten times the weight of anhydrous arsenious acid, the acid is completely removed from the liquid. With a smaller proportion of ferric oxide, the precipitation is nearly though not quite complete. The products formed are basic arsenites containing $3Fe^4O^3.As^2O^3$, &c., from which part of the arsenious acid may be extracted by water. It is this power possessed by hydrated ferric oxide of removing arsenious acid from a solution, which renders it so useful as an antidote to arsenious acid (p. 374).

Arsenious acid, or arsenite of potassium, forms with ferric acetate an ochre-yellow precipitate, which dries up to a brown mass containing $4Fe^2O^3.As^2O^3 + 5Aq$, and when heated gives off water and the greater part of the acid (Bunsen), the whole, according to Simon. Water removes part of the arsenious acid; strong mineral acids dissolves the salt completely. Ferric sulphate or chloride is not precipitated by free arsenious acid: but gives with arsenite of potassium, according to Guibourt, a rusty-brown precipitate, containing when dry, $2Fe^4O^3.As^2O^3 + 7H^2O$. According to Damour, this precipitate is slowly dissolved, with rusty-brown colour, by caustic potash, and when slowly heated, melts before giving off arsenious oxide. A rusty yellow precipitate, likewise containing $2Fe^4O^3.As^2O^3 + 7H^2O$, is obtained by oxidising a solution of ferrous sulphate with aqua-regia, neutralising with ammonia, and precipitating by soda-ley, which has been saturated at the boiling heat with arsenious acid and freed from the excess of that acid by cooling. It is soluble in caustic soda, and the solution, evaporated to dryness, yields a red mass perfectly soluble in water.

Ferrous Arsenite, $2Fe^2O.As^2O^3$, is obtained by mixing ferrous sulphate with a solution of arsenious acid in ammonia, as a greenish white precipitate, which becomes ochre-yellow on drying. The non-oxidised compound is soluble in ammonia.

Arsenite of Lead.—The *neutral* salt, $Pb^2O.As^2O^3$, or $PbAsO^2$, is obtained by precipitating neutral acetate of lead with acid arsenite of potassium, or with arsenious acid (Filhol), or, according to Berzelius, with ammonia which has been saturated with arsenious acid while warm; the precipitate obtained by the latter process contains water, becomes strongly electrical by friction, and when heated gives off some of its acid and water, and melts to a yellowish glass. Neutral arsenite of lead is somewhat soluble in water, insoluble in potash, but soluble in soda. The *tetraplumbic* salt, $Pb^4As^2O^5$, or $2Pb^2O.As^2O^3$, is formed, according to Filhol, by precipitating neutral acetate of lead with basic arsenite of potassium, or, according to Berzelius, by precipitating basic acetate of lead with an ammoniacal solution of arsenious acid. It is a white hydrated powder, insoluble in water and in ammonia-salts, melting to a yellowish glass when heated. According to Simon, it is obtained by passing the vapour of arsenious oxide over red-hot oxide of lead, as a sulphur-yellow, easily fusible glass which sustains a considerable degree of heat without decomposing. A *triplumbic salt*, $3Pb^2O.As^2O^3$, or Pb^3AsO^3, is obtained by precipitating basic acetate of lead with a boiling solution of arsenious acid. (Kühn.)

Arsenite of Magnesium.—Calcined magnesia, boiled with arsenious acid, takes up a portion of it, but not in any definite amount. A precipitate of uncertain composition is obtained by mixing sulphate of magnesium with acid arsenite of potassium, and heating. A solution of sulphate of magnesium is not precipitated by aqueous arsenious acid; but on adding a small quantity of ammonia, a copious precipitate is formed which, according to Stein, has, after drying over sulphuric acid, the composition Mg^3AsO^3, or $3Mg^2O.As^2O^3$. It is insoluble in ammonia, but dissolves in a large excess of sal-ammoniac. (H. Rose.)

Arsenite of Manganese, $3Mn^2O.2As^2O^3 + 5H^2O$, is obtained, by treating a manganous solution with arsenite of ammonium, as a rose-coloured precipitate, which oxidises rapidly in the air, gives off 1 at. water at 100° C., and at a higher temperature gives off arsenious oxide and metallic arsenic, leaving a residue of manganese and manganous arsenate.

Arsenites of Mercury.—The *mercuric* salt is obtained, by precipitating mercuric nitrate with arsenious acid, as a white powder soluble in nitric acid. It dissolves also in arsenite of potassium, and if the solution contains excess of potash, a black deposit of reduced metal is immediately formed. The *mercurous* salt is obtained by double decomposition, or by digesting mercury in arsenic acid, as a white precipitate soluble in nitric acid.

Arsenite of Nickel.—The salt $2Ni^2O.As^2O^3$ is precipitated on adding arsenite of potassium to a nickel-salt. A less basic salt, $3Ni^2O.2As^2O^3 + 4H^2O$, is produced, according to Girard (Compt. rend. xxxiv. 918), by quickly mixing a solution of chloride of nickel containing a large excess of sal-ammoniac, with arsenite of potassium. It is a greenish precipitate, which gives off 10·3 per cent. (4 at.) water at 110° C. When heated in the air, it first gives off its water, and then yields a sublimate of arsenious oxide, leaving yellow infusible arsenate of nickel:

$$3Ni^2O.2As^2O^3 + O^2 = 3Ni^2O.As^2O^5 + As^2O^3.$$

Arsenite of nickel dissolves with violet colour in ammonia. It is converted by nitric acid into arsenate; by hydrochloric acid into arsenious acid and chloride of nickel.

Arsenite of Potassium.—The *neutral* or *monopotassic salt*, $KAsO^2$, or $K^2O.As^2O^3$, is obtained, by boiling the acid salt for some time with carbonate of potassium, and agitating the residual salt several times with alcohol: it then remains as a syrupy mass (Pasteur). Filhol was not able to prepare it pure. An *acid salt*, $K^2O.2As^2O^3 + 2H^2O$, is obtained, by boiling potash-ley with excess of arsenious acid, whereby an alkaline liquid is produced, which gives with silver-salts a yellow precipitate, $2Ag^2O.As^2O^3$, mixed with arsenious acid, the liquid at the same time becoming acid. On mixing the alkaline liquid with alcohol, it becomes thick and turbid, deposits after a few days right rectangular prismatic crystals, adhering to the sides of vessel and after a longer time solidifies completely to a saline mass. The salt gives off 1 at. water at 100° C., whence it should perhaps be regarded as $2KHAs^2O^4 + H^2O$ (Pasteur). The *basic* or *tetrapotassic salt*, $2K^2O.As^2O^3$, is obtained by mixing the neutral salt with excess of potash-ley and precipitating by alcohol. It is very soluble in water, and yields with silver-salts a yellow precipitate of the diargentic salt, $2Ag^2O.As^2O^3$, the liquid remaining neutral.

Arsenite with Iodide of Potassium.—A solution of iodide of potassium yields with arsenious acid or arsenite of potassium, a precipitate, $2KI.3As^2O^3$, which is sparingly soluble in cold water, dissolves in 19 pts. of boiling water, and decomposes at 315° C., when heated with sulphuric acid (Emmet, Sill. Am. J. [2] xviii. 583). By passing carbonic acid gas into a solution of this salt in a small quantity of boiling water mixed with 3 or 4 times its volume of hot alcohol, and evaporating the resulting syrupy liquid, a crystallised compound is obtained, consisting of $2KI . 3(K^2O.H^2O.As^2O^3)$, or $2(KI.3KAsO^2) + 3H^2O$. This salt is soluble in water and in alcohol, and reacts with metallic salts like a mixture of iodide and arsenite of potassium. Strong sulphuric acid decomposes it, forming a red or yellowish precipitate of arsenious iodide. The hot saturated solution of this salt deposits on cooling, nodular masses, or, when carbonic acid gas is passed through it, a white powder, consisting of the salt $2KI.(K^2O.H^2O.3As^2O^3)$, or $2(KI.KHAs^2O^4).As^2O^3$, which is sparingly soluble in water, and when heated in a narrow glass tube, gives off vapour of water and metallic arsenic, together with arsenious oxide. No iodine is given off unless the air has access to the salt. (E. Harms, Ann. Ch. Pharm. xci. 371.)

Arsenite of Silver.—The *tetrargentic* salt, $2Ag^2O.As^2O^3 = Ag^4As^2O^5$, is formed as a yellow precipitate on treating solutions of silver salts with alkaline arsenites (pp. 361, 375). It gradually turns dark grey when exposed to the air, blackens if exposed to light. When heated, it gives off, according to Simon, first water, then arsenious oxide, and leaves a mixture of arsenate of silver with metallic silver.

Another arsenite of silver is obtained, according to Filhol, as a light yellow precipitate on adding ammonia saturated with arsenious acid to an ammoniacal solution of nitrate of silver. Between 140° and 150° C. it blackens suddenly, without loss of weight, and at a higher temperature melts and gives off arsenious oxide.

It is easily soluble in acetic acid (whereby it is distinguished from phosphate of silver); soluble also in potash. The latter solution is not precipitated by chloride of potassium, but, on the contrary, is capable of dissolving an additional quantity of chloride of silver. It slowly deposits metallic silver, while arsenate of potassium remains in solution. When a solution of chloride of palladium or platinum is mixed with arsenite of potassium, and then with arsenite of silver and potassium, the platinum or palladium separates quickly in the metallic state. (Reynoso.)

Sesqui-argentic Arsenite, $3Ag^2O.2As^2O^3$, or $Ag^2O.4(AgAsO^2)$, is produced as a white precipitate, with evolution of ammonia, when nitrate of silver, mixed with a large excess of nitrate of ammonium, is added by drops to arsenite of potassium. It is blackened by light, dissolves in ammonia and in excess of arsenite of potassium, and when heated blackens, yields a sublimate of arsenious oxide, and leaves a fusible residue of a fine red colour. (E. Harms and others.)

Arsenite of Sodium.—According to Pasteur, the sodium-salts of arsenious acid correspond exactly to the potassium-salts, excepting that the acid salt does not crystallise. Filhol did not obtain the neutral salt in a state of purity.

Arsenite of Strontium, $SrAsO^2 + 2H^2O$.—Strontia-water is not precipitated by aqueous arsenious acid in any proportion, even on boiling (Gmelin). Chloride of strontium is precipitated by arsenite of potassium, but only after some days. The precipitate gives off one-fourth of its water at 100° C.

Arsenites of Tin.—Both the *stannic* and the *stannous* salts are white precipitates; the former is difficult to fuse.

ARSENIC OXIDE, As^2O^5, or AsO^5. In the hydrated state, **ARSENIC ACID.**—This compound is produced by oxidising arsenious oxide or arsenious acid with nitric acid, aqua-regia, hypochlorous acid, or other oxidising agents.—1. When 4 parts of arsenious oxide are gradually added to 3 pts. of nitric acid of specific gravity 1·35, the mixture becomes hot, and after 24 hours yields a syrupy liquid like strong oil of vitriol, consisting of arsenic acid, still containing a little arsenious acid, which may be completely oxidised by the addition of a small quantity of nitric acid. This process is used for the preparation of arsenic acid on the large scale (E. Kopp).—2. Four parts of arsenious oxide are heated with 1 pt. of hydrochloric acid, 12 pts. of nitric acid are gradually added (Mitscherlich), and the resulting solution is evaporated to a syrup. Both the oxidation and evaporation must be performed under a chimney having a good draught, because part of the arsenic is converted into chloride, which escapes in vapour.—3. Arsenic acid is also produced, together with hydrochloric acid, by passing chlorine gas into aqueous arsenious acid.

Arsenic acid forms three hydrates analogous to those of phosphoric acid, viz.:

Monohydrate . . $H^2O.As^2O^5$, or $HAsO^3 = \left.\begin{matrix}(AsO^2)'\\ H\end{matrix}\right\}O$ *

Dihydrate . . $2H^2O.As^2O^5$, or $H^4As^2O^7 = \left.\begin{matrix}\overset{iv}{(As^2O^3)}\\ H^4\end{matrix}\right\}O^4$

Trihydrate . . $3H^2O.As^2O^5$, or $H^3AsO^4 = \left.\begin{matrix}(AsO)'''\\ H^3\end{matrix}\right\}O^3$

The syrupy solution obtained as above, deposits, after standing for some time at 15° C. (60° F.), transparent, rather long prisms or rhomboïdal laminæ, containing $3H^2O.As^2O^5 + H^2O$, or $2H^3AsO^4 + H^2O$;—they deliquesce rapidly in the air, and dissolve in water with great reduction of temperature. Both the water of crystallisation and the basic water may be expelled by heat.

The crystals heated to 100° C., first melt, and then yield the *trihydrate*, H^3AsO^4, as a crystalline precipitate. The same compound may be obtained in large transparent crystals by exposing a concentrated solution of arsenic acid to a very low temperature.

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* If $O = 8$, the formulæ are $HO.AsO^5$, $2HO.AsO^5$, and $3HO.AsO^5$.

It dissolves easily in water, without reduction of temperature. The *dihydrate*, $H^4As^2O^7$, which may be regarded as a compound of the mono- and tri-hydrates, is obtained by heating the crystallised acid, $2H^3AsO^4.H^2O$, for some time to 140°—160° C.; it then separates in hard shining crystals, leaving a mother-liquor of specific gravity 2·36 at 16° C. It dissolves in water with moderate facility, but the solution is attended with great rise of temperature.

The *monohydrate*, $HAsO^3$, is formed by heating the before-mentioned crystals to 200°, and at last to 206° C.; the mass then suddenly becomes pasty, gives off a large quantity of aqueous vapour, and is ultimately converted into a white nacreous substance consisting chiefly of the monohydrate; it dissolves slowly in cold water, with moderate facility in warm water, producing great evolution of heat. (E. Kopp, Ann. Ch. Phys. [3] xlviii. 196.)

Arsenic Oxide, Arsenic Anhydride, Anhydrous Arsenic Acid, Pentoxide of Arsenic, As^2O^5, is obtained by heating either of the hydrates to dull redness, and remains in the form of a white mass, which has no action upon litmus; is nearly insoluble in water, and in ammonia; and scarcely absorbs water from moist air, even in the course of several days, deliquescing only after a long time. At a full red heat, it is resolved into arsenious oxide and free oxygen.

The solutions of the three hydrates and of the anhydride exhibit exactly the same characters; they have a sour metallic taste, and all contain the trihydrate, the other hydrates being immediately converted into that compound when dissolved in water: in this respect, the hydrates of arsenic acid differ essentially from those of phosphoric acid.

Arsenic oxide is reduced to the metallic state by *charcoal*, *metals*, *cyanide of potassium, &c.*, at a red heat, in the same manner as arsenious oxide. Aqueous arsenic acid dissolves *zinc* and *iron*, with evolution of pure hydrogen; but if sulphuric or hydrochloric acid is present, the arsenic acid is reduced, metallic arsenic, and solid arsenide of hydrogen are deposited, and arsenetted hydrogen gas is evolved (p. 363). An *electric current* passed through aqueous arsenic acid acidulated with sulphuric or hydrochloric acid eliminates arsenetted hydrogen, provided the solution does not contain chlorides (Bloxam). *Sulphurous acid* reduces arsenic acid to arsenious acid, with formation of sulphuric acid. *Hydrosulphuric acid* slowly precipitates trisulphide of arsenic, the action being assisted by heat, or by the presence of another acid. *Hyposulphite of sodium* added to a solution of arsenic acid containing hydrochloric acid, likewise throws down trisulphide of arsenic mixed with sulphur:

$$5Na^2S^2O^3 + 2H^3AsO^4 = As^2S^3 + S^2 + 5Na^2SO^4 + 3H^2O.$$

Arsenic acid and its salts are very poisonous, but not in so high a degree as arsenious acid and the arsenites (Wöhler and Frerichs, Ann. Ch. Pharm. lxv. 335). A strong solution of arsenic acid placed upon the skin produces blisters like burns.

Arsenic acid is now extensively used in calico printing, in place of tartaric acid, for developing white patterns on a coloured ground in the chloride-of-lime vat.

Arsenates.—Arsenic acid is a strong acid, expelling all the more volatile acids from their salts at high temperatures. It is tribasic like ordinary phosphoric acid, the general formula of its salts being M^3AsO^4, in which 1 or 2 at. M may be replaced by hydrogen. The solutions of the *tri*- and *di*-metallic salts, M^3AsO^4, and M^2HAsO^4; (sometimes called *basic* and *neutral*) have an alkaline or neutral reaction; those of the *mono*-metallic (or *acid*) salts, MH^2AsO^4, have an acid reaction. The di- and monometallic arsenates give off their water when heated, but take it up again on being dissolved in water: consequently there are no arsenates corresponding to the pyro- and meta-phosphates.

The arsenates of the alkali-metals are soluble in water; of the others, only the monometallic salts are soluble in water; but the di- and tri-metallic salts dissolve readily in free arsenic acid, and in the stronger mineral acids, less easily in acetic acids: hence solutions of salts of the earth-metals and heavy metals are precipitated by arsenate of potassium, but not by free arsenic acid.

The dimetallic arsenates of barium, strontium, and calcium, are insoluble in water, but soluble in ammoniacal salts; hence solutions containing arsenic acid together with large quantities of ammoniacal salts are not precipitated by the salts of barium, strontium, and calcium. When solutions of metallic salts are precipitated by a dimetallic arsenate of an alkali-metal, an insoluble trimetallic arsenate, M^3AsO^4, is often formed, the liquid at the same time acquiring an acid reaction.

A solution of an arsenate in hydrochloric acid is slowly precipitated by *sulphuretted hydrogen*, the precipitate consisting of trisulphide of arsenic and sulphur in the proportion of the pentasulphide; and if the metallic base of the salt is likewise thrown down by sulphuretted hydrogen from an acid solution, a precipitate is formed consisting of a metallic sulpharsenate. A solution of an *alkaline sulphide*, with subsequent addition of hydrochloric acid, acts in the same manner as sulphuretted hydrogen. An aqueous solution of an arsenate boiled with *hyposulphite of sodium*, deposits trisulphide of arsenic and sulphur on addition of hydrochloric acid. *Potash* withdraws from the insoluble arsenates the whole or part of the arsenic acid.

Solutions of the tri- and di-metallic arsenates of alkali-metal give white precipitates with *baryta-* or *lime-water*, also with salts of *barium*, *strontium*, *calcium*, the *earth-metals*, *manganese*, *zinc*, and *lead*, also with *stannous* and *ferric* salts; yellowish-white with *uranic* and *mercurous* salts, yellow with *mercuric*-salts; rose-coloured with *cobalt*-salts, green with *nickel*-salts; pale greenish blue with *cupric* salts; light brown with *platinic* salts; brown-red with *silver*-salts. These precipitates are for the most part soluble in arsenic, sulphuric, hydrochloric, and nitric acid, and in ammoniacal salts: arsenate of silver, however, is not soluble in ammoniacal salts.

Magnesium-salts mixed with sufficient chloride of ammonium to prevent precipitation by ammonia, give with solutions of arsenates, a white crystalline precipitate of arsenate of magnesium and ammonium, insoluble in aqueous ammonia and in chloride of ammonium; the latter character distinguishes it from the corresponding salt of arsenious acid (p. 377).—Solutions of arsenates added to excess of *molybdate* of ammonium containing nitric acid, form, when the liquid is heated, a bright yellow precipitate of arseno-molybdate of ammonium.—All arsenates dissolved in water or in nitric acid, give with *basic acetate of lead*, a white precipitate of arsenate of lead, which when ignited with charcoal, melts and is reduced, with abundant evolution of metallic arsenic. The last three reactions afford very delicate tests for arsenic acid. The reaction with uranic salts is also very delicate, being perceptible to the twenty-thousandth degree of dilution.

The arsenates are isomorphous with the corresponding phosphates.

Arsenate of Aluminium, $2Al^4O^3.3As^2O^5$, is obtained by double decomposition as a white precipitate, easily soluble in free acid, and remaining as a vitreous mass when the solutions are evaporated.

Arsenate of Ammonium.—The *triammonic* salt, $(NH^4)^3AsO^4$, is obtained by supersaturating a strong solution of arsenic acid with ammonia, as a heavy soluble powder, which, when slightly heated, is quickly converted into the following salt:—The *diammonic* salt, $(NH^4)^2.H.AsO^4$, is formed in the manner just mentioned, and also by saturating a strong solution of arsenic acid with ammonia till a precipitate begins to form; by leaving the solution to evaporate, it is obtained in prismatic crystals of the trimetric system, which effloresce in the air, giving off half their ammonia, but no water. When heated, it decomposes, yielding metallic arsenic, ammonia, water, and nitrogen gas. Its solution has an alkaline reaction. The *monammonic* or *acid* salt, $NH^4.H^2.AsO^2$. is obtained by imperfectly saturating arsenic acid with ammonia. It is deliquescent, very soluble in water, and separates from the solution by spontaneous evaporation in square-based octahedrons. It is decomposed by heat like the preceding. Its solution has a strong acid reaction.

Arsenate of Barium.—The *tribarytic* salt, Ba^3AsO^4, is obtained as a white powder, nearly insoluble in water, by precipitating aqueous arsenic acid with baryta-water (Laugier), or better, by gradually dropping trisodic arsenate into chloride of barium (Graham). The *dibarytic* salt, $2Ba^2HAsO^4$, is obtained when a solution of the disodic salt is added drop by drop to an excess of chloride of barium. If, on the other hand, the arsenate of sodium is in excess, the precipitate formed is a mixture of the di- and tri-barytic salts, while monobarytic arsenate remains in solution. The di-barytic salt contains, according to Mitscherlich, $\frac{1}{2}$ at. water $(2Ba^2HAsO^4 + H^2O)$; according to Berzelius, 2 at. It gives up its water at a red heat. In contact with water, it is resolved into the monobarytic salt, which dissolves, and the tribarytic salt which remains undissolved (Berzelius). The *monobarytic* salt, BaH^2AsO^4, is obtained by adding baryta-water to aqueous arsenic acid till a precipitate begins to form; also by treating the dibarytic salt with water, or better, by dissolving it in aqueous arsenic acid, and leaving the solution to crystallise. If a very large excess of arsenic acid be used, the solution evaporated nearly to dryness, and the mass treated with water, there remains a white powder, consisting of an acid salt containing $Ba^2O.3H^2O.2As^2O^5 + 2H^2O$, or $2BaH^2AsO^4.As^2O^5 + 3H^2O$. (Setterberg.)

Arsenate of Barium and Ammonium, $Ba^2(NH^4)AsO^4 + \frac{1}{2}H^2O$, is obtained by mixing the dibarytic salt with ammonia (Baumann), and $Ba(NH^4)HO^4$, by mixing a solution of nitrate of barium with arsenic acid (Mitscherlich); both salts are formed as bulky precipitates, which become crystalline after a while.

Arsenate of Calcium.—The *dicalcic salt* occurs native, as *Haidingerite*, $2Ca^2HAsO^4 + H^2O$, and *Pharmacolite*, $2Ca^2HAsO^4 + 5H^2O$, and may be prepared like the corresponding barium-salt. The *monocalcic salt* is soluble, the *tricalcic salt* insoluble in water; the latter is obtained by precipitating chloride of calcium in excess with trisodic arsenate. (Graham.)

Arsenate of Calcium and Ammonium, $Ca^2(NH^4)AsO^4 + 6H^2O$, is produced, according to Wach (Schw. J. xii. 285), by mixing a hot solution of arsenic acid in excess of ammonia, with nitrate of calcium, and crystallises on cooling in tables arranged like steps; if the solutions are mixed cold, the salt is precipitated as a powder. Any arsenious acid that may be present remains dissolved. Another salt $Ca(NH^4)HAsO^4$ is obtained by adding ammonia in excess to a solution of dicalcic arsenate in nitric acid, as a flocculent precipitate, soon changing to a mass of needle-shaped crystals. If only enough ammonia be added to precipitate a portion of the salt, and the remaining liquid be left at rest, the same salt is obtained in crystals belonging to the regular system: it is therefore dimorphous. (Baumann.)

Cerous Arsenate, $2Ce^2O.As^2O^5$ (?), is a white powder insoluble in water, but dissolving in arsenic acid as an acid salt, which dries up to a vitreous mass. (Hisinger and Berzelius.)

Chromic Arsenate.—*Chromic* salts yield with arsenate of potassium an apple-green precipitate.

Arsenates of Cobalt.—The *cobaltic* salt is a brown precipitate, obtained by adding arsenate of potassium to a solution of cobaltic hydrate in acetic acid.

Cobaltous Arsenate.—The *tricobaltous salt* occurs in red crystals, as *cobalt-bloom*, $Co^3AsO^4.4H^2O$ (Kersten), a secondary product formed by the weathering of cobaltine (see COBALT-BLOOM); and is obtained artificially as a reddish powder by precipitating cobalt-salts with trisodic arsenate.

A basic arsenate of cobalt, known in commerce as *Chaux métallique*, is prepared: 1. By adding carbonate of potassium to a solution of cobalt-glance in nitric acid or aqua-regia, as long as a white precipitate of ferric arsenate continues to form, then filtering, and treating the filtrate with more carbonate of potassium to precipitate cobaltous arsenate.—2. By fusing cobalt-glance with twice its weight of crude potash and a little quartz-sand, exhausting the fused mass with water, which takes up sulphide of potassium, together with arsenic, iron, and potassium, and again fusing the white regulus with potash, whereby a blue slag is obtained, which is used for the preparation of smalt, and a pure regulus of arsenide of cobalt, which, by careful roasting, is converted into the required basic arsenate.

The product obtained by either of these processes is a reddish powder, which dissolves in ammonia with bluish-red, or in hydrochloric acid with red colour. Caustic potash extracts the arsenic acid and leaves a blue protoxide of cobalt, which, when ignited with 1 or 2 pts. of alumina yields a fine blue pigment.

Gentele, by melting *Chaux métallique*, prepared in the wet way, in a porcelain furnace, obtained a mass, the cavities of which contained deep blue prisms, yielding a rose-coloured powder, easily soluble in acids, and consisting of $4Co^2O.As^2O^5$.

The *dicobaltous* salt is not known. The *monocobaltous* salt is obtained by evaporating in vacuo the solution of cobaltous hydrate in excess of arsenic acid.

Arsenate of Copper, Cu^3AsO^4, is obtained as a green powder by precipitating sulphate of copper with disodic arsenate, the liquid at the same time becoming acid. If the liquid, together with the precipitate, be mixed with a sufficient quantity of ammonia to dissolve the precipitate, and the solution be then left to evaporate, crystals are obtained, consisting of $Cu(NH^4)^2AsO^4 + NH^4.H.O$, which are permanent in the air at ordinary temperatures, but are decomposed by exposure to sunshine, or by a temperature of 300° C., ammonia and water first passing off, and arsenious oxide subliming at higher temperatures.

Several *basic* arsenates of copper occur as natural minerals, viz. $4Cu^2O.As^2O^5$, occurring with 1 at. water as *olivenite*, with $7H^2O$ as *euchroite*, and with $10H^2O$ as *liroconite;* also $5Cu^2O.As^2O^5$, occurring with $2H^2O$ as *erinite*, with $5H^2O$ as *aphanese*, and with $10H^2O$ as *leirochroite* (*Kupferschaum*).

Arsenate of Iridium.—Brown precipitate formed on adding arsenate of sodium to chloride of iridium, and heating.

Arsenates of Iron.—A *ferric arsenate*, $2Fe^4O^3.3H^2O.3As^2O^5 + 9Aq$, or $fe^2HAsO^4 + 3Aq$, is obtained by precipitating ferric chloride with disodic arsenate, as a white powder, which turns red and gives off water when heated. At a red heat it glows slightly, and acquires a more yellowish tint. It dissolves in hydrochloric and in nitric acid, separating as a white powder on evaporation. It is insoluble in acetic acid and in ammoniacal salts. Aqueous ammonia dissolves it immediately when recently precipitated, slowly after drying. The solution when evaporated leaves a ruby-red, transparent, fissured mass, consisting of *ammonio-ferric arsenate*, soluble in ammonia, but decomposed by pure water, which extracts arsenate of ammonium, together with the undecomposed portion of the salt, and leaves ferric arsenate. The ammoniacal solution remains clear when mixed with ferrocyanide of potassium, but on addition of an acid yields Prussian blue. When diferrous arsenate is oxidised with nitric acid and ammonia is added in excess, a precipitate is formed consisting of $Fe^4O^3.As^2O^5$, or fe^3AsO^4, insoluble in ammonia. Potash in large excess extracts part of the acid, leaving a compound of 7 pts. arsenic acid (anhydrous) with 79 pts. ferric oxide, corresponding to the formula $16Fe^4O^3.As^2O^5 + 24H^2O$ (Berzelius). On heating this salt to redness, bright incandescence takes place, but no arsenious oxide is given off.

Iron-cinder is a native ferric arsenate containing $2Fe^4O^3.As^2O^5 + 12H^2O$; *scorodite* is $Fe^4O^3.As^2O^5 + 4H^2O$ or $fe^3AsO^4 + 2H^2O$; *cube-ore* is a *ferroso-ferric arsenate* = $Fe^2O.Fe^4O^3.As^2O^5 + 6H^2O$; *pittizite* or *brown iron ore* is a ferric arsenate, $2Fe^4O^3.As^2O^5 + 12H^2O$, combined, or perhaps only mixed, with ferric sulphate and water.

b. *Ferrous Arsenate* is obtained by precipitation as a white powder, which assumes a dirty green colour when exposed to the air.

Arsenate of Lead.—The *triplumbic* salt, Pb^3AsO^4, is prepared by dropping a solution of a lead-salt into excess of disodic arsenate, or by digesting the diplumbic salt with ammonia. When heated, it turns yellow and cakes together, but does not melt. Insoluble in ammonia and ammoniacal salts. A *tetraplumbic* salt, $2Pb^2O.As^2O^5$, or $Pb^4As^2O^7$, is precipitated on mixing a solution of nitrate of lead with arsenic acid, or with less than the equivalent quantity of di-ammonic, dipotassic, or disodic arsenate. It is a white crystalline powder, insoluble in water and in acetic acid, soluble in nitric and in hydrochloric acid.

Arseno-chloride of Lead.—In many varieties of *pyromorphite*, $PbCl.3Pb^3PO^4$, the phosphorus is more or less replaced by arsenic.

Arsenate of Magnesium.—The *trimagnesic* salt, Mg^3AsO^4, is formed by precipitating sulphate of magnesium with disodic arsenate, or by boiling the dimagnesic salt for a long time with a strong solution of arsenate of sodium.—The *dimagnesic* salt, $2Mg^2HAsO^4 + 13H^2O$ (Graham), is formed as a white insoluble precipitate on mixing the dilute solutions of 3 pts. sulphate of magnesium, and 5 pts. disodic arsenate. In the recent state, it dissolves easily in nitric acid, but it is insoluble in acids after ignition. The *monomagnesic* salt dissolves readily in water, and dries up to a gummy mass.

Arsenate of Magnesium and Ammonium, $Mg^2(NH^4)AsO^4 + 6H\ O$, is obtained as a crystalline precipitate by adding arsenic acid strongly supersaturated with ammonia to a solution of a magnesium-salt mixed with sal-ammoniac. At 100° C. it gives off $\frac{11}{12}$ of its water (44·28 per cent.), together with ammonia and a certain portion of arsenic. Like the corresponding phosphate, it is almost insoluble in water containing ammonia, or in sal-ammoniac, and is therefore well adapted for the estimation of arsenic acid, and for separating that acid from arsenious acid. (H. Rose, p. 367.)

An *arsenate of Magnesium and Calcium*, containing $Ca^2HAsO^4.Mg^2HAsO^4 + Ca^3AsO^4.Mg^3AsO^4 + 5H^2O$, occurs native as *picropharmacolite.*

Arsenate of Magnesium and Potassium, Mg^2KAsO^4, is produced by fusing arsenate of magnesium with excess of carbonate of potassium, and adding 1 at. hydrate of potassium: it is easily decomposed by water. The corresponding *sodium-salt* is obtained in like manner.

Arsenate of Manganese, Mn^2HAsO^4, is obtained by saturating arsenic acid with recently precipitated carbonate of manganese.

Arsenate of Manganese and Ammonium, $Mn^2(NH^4)AsO^4 + 6H^2O$.—Reddish-white precipitate, gummy at first, afterwards becoming crystalline: obtained like the corresponding magnesium-salt.

Arsenates of Mercury.—A *mercuric arsenate* is obtained as a yellow precipitate on adding arsenic acid to mercuric nitrate, or arsenate of sodium to mercuric chloride. The same yellow salt is produced, with volatilisation of arsenious oxide, when arsenic oxide is heated with mercury.

Di-mercurous arsenate, $2Hg^4O.H^2O.As^2O^5 + H^2O$, or $Hhg^2.H.AsO^4 + \frac{1}{2}H^2O$ *, is obtained by dropping mercurous nitrate into a strong solution of arsenic acid, as a white precipitate, which turns red in drying. When, on the other hand, arsenic acid or arsenate of sodium is added to the mercurous solution, a double salt of arsenate and nitrate of mercurosum is first formed; but it quickly decomposes, especially if heated, assuming a yellow, orange, red, and ultimately purple tint. When either of these precipitates is dissolved in warm nitric acid, and the acid is gradually neutralised with ammonia, a black precipitate is formed, which turns red when heated for some time.

Dimercurous arsenate is composed of fine needles, sometimes brown-red, sometimes purple-red. When dried at 100° C., and then more strongly heated, it first gives off

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* Hhg = Hg = 200.

a little water, then mercury, and leaves yellow mercuric arsenate, which, at a higher temperature, is resolved into mercury, arsenious oxide, and free oxygen. With cold concentrated hydrochloric acid, it yields a solution of arsenic acid, and a residue of calomel, which is resolved by boiling into mercury and soluble mercuric chloride. It is converted into mercuric arsenate by boiling with nitric acid, but dissolves unchanged in that acid when cold, the solution being precipitated by ammonia. It dissolves slightly in aqueous nitrate of ammonium, and separates on evaporation with fine red colour and crystalline structure. It is quite insoluble in water, acetic acid, and ammonia. (Simon, Pogg. Ann. xli. 424.)

Monomercurous arsenate, $HhgAsO^3$, or $Hg^4O.As^2O^5$, is produced by boiling mercuric oxide, or the di-mercurous salt, to dryness with aqueous arsenic acid, triturating the dry mass when cold with water, washing the powder, and drying it over the water-bath, whereby the whole of the water is expelled. It is white and amorphous, gives off mercury at a red heat, and leaves mercuric arsenate, which then undergoes further decomposition. By careful addition of potash, it is converted into the dimercurous salt. With hydrochloric acid and with boiling nitric acid, it behaves like the dimercurous salt. In cold nitric acid it dissolves less abundantly than the latter, and on heating with gradual addition of ammonia, it yields a precipitate of the dimercurous salt. It is insoluble in water, acetic acid, and alcohol. (Simon.)

A double salt, consisting of *arsenate* and *nitrate of mercurosum*, $Hhg^4As^2O^7.2HhgNO^3$ is obtained, when water is carefully poured upon an equal volume of a strong solution of mercurous arsenate in moderately strong nitric acid, and an equal volume of aqueous ammonia then added, without allowing the liquids to mix. The double salt is then gradually deposited in white nodules and needles. If the mercurous nitrate be mixed with a very small quantity of nitric acid, the compound is obtained in the form of powder. (Simon.)

Arsenate of Molybdenum.—*Molybdous Arsenate* is a grey precipitate, produced by mixing molybdous chloride with arsenate of sodium. The precipitate redissolves at first, but afterwards becomes permanent.

Arseno-molybdic Acid.—Arsenic and molybdic acids digested together yield a colourless acid solution, and a lemon-yellow basic salt, insoluble in water. The solution evaporated to a syrup, yields colourless crystals, which when treated with alcohol, first yield white flocks, and then dissolve.

Arseno-molybdate of Ammonium.—On adding arsenic acid to a solution of molybdate of ammonium and heating to 100° C., a yellow precipitate is formed, similar to that produced by phosphoric acid. It contains 7 per cent. arsenic, and appears to be analogous to phospho-molybdate of ammonium. (See PHOSPHORIC ACID.)

Arsenate of Nickel, Ni^3AsO^4, occurs as *nickel-bloom*, and is obtained by double decomposition as an apple-green crystalline powder, insoluble in water, soluble in arsenic acid and in other strong acids, also in ammonia; from the latter solution potash throws down hydrate of nickel free from arsenic.

Arsenate of Palladium.—Light yellow precipitate obtained by heating together the solutions of neutral nitrate of palladium and arsenate of sodium.

Arsenate of Platinum.—Light brown powder soluble in nitric acid, obtained by precipitating platinic nitrate with arsenate of sodium.

Arsenate of Potassium.—The *tripotassic* salt, K^3AsO^4, is obtained, by mixing aqueous arsenic acid or the neutral salt with potash-ley, and strong concentration, in small needles, which deliquesce quickly in the air. The *dipotassic salt*, K^2HAsO^4, is a deliquescent non-crystalline mass, produced by saturating arsenic acid with potash, or by fusing arsenious oxide with hydrate of potassium.

The *monopotassic salt*, KH^2AsO^4 (Macquer's *arsenikalisches Mittelsalz*), is prepared: 1. By deflagrating arsenious oxide with an equal weight of nitre, dissolving the fused mass in water, and leaving the solution to crystallise.—2. By mixing aqueous carbonate of potassium with such a quantity of arsenic acid, that the solution reddens litmus-paper but the redness disappears as the paper dries, and then evaporating.—3. A mixture of potash-ley and arsenic acid neutral to vegetable colours, deposits the monopotassic salt when partially evaporated, the alkaline dipotassic salt remaining in solution (Mitscherlich). Monopotassic arsenate is isomorphous with the corresponding phosphates of potassium and ammonium, and with monammonic arsenate. The crystals have a specific gravity of 2·638; they are permanent in the air, and give off but little water, even at 288° C., but at a red heat they melt, give off water, and are converted into a thin liquid, which on cooling solidifies into a white mass, cracked in all directions. They dissolve in 5·3 pts. of water at 6° C., forming a solution of specific gravity, 1·1134; they are much more soluble in hot water, but insoluble in alcohol. The aqueous solution reddens litmus, but the redness disappears on drying.

It does not precipitate the salts of barium, calcium, magnesium, or the other earth-metals.

Arsenate of Rhodium.—Yellowish-white precipitate formed by heating arsenate of sodium with chloride of rhodium and sodium.

Arsenate of Silver.—The *tri-argentic salt*, Ag^3AsO^4, is the only one that can be obtained by precipitating nitrate of silver with soluble arsenates; it is a dark brown precipitate which melts to a brown-red glass when heated, is converted into chloride of silver by hydrochloric acid, dissolves in acetic acid and aqueous ammonia, and when heated, in sulphate, nitrate and succinate of ammonium. It dissolves also in aqueous arsenic acid, and the solution, if left to evaporate, deposits the *monargentic* salt, AgH^2AsO^4. Both this salt and the mother-liquor from which it has separated, are decomposed by water, yielding the brown triargentic salt.

The triargentic salt treated with sulphuric acid yields by evaporation a double salt, $Ag^4As^2O^7.Ag^2SO^4$, which is decomposed by water and by dilute sulphuric acid. (Setterberg.)

Arsenate of Sodium.—The *trisodic salt*, $Na^3AsO^4 + 12H^2O$ is prepared by fusing 1 at. of the disodic salt with carbonate of sodium, or by mixing the aqueous solution of arsenic acid with excess of carbonate of sodium, and evaporating to a small bulk. The salt then crystallises almost completely, the excess of soda remaining dissolved. The crystals are right rhombic prisms permanent in the air; they have an alkaline taste, melt at 86° C., and dissolve in $3\frac{1}{2}$ pts. of water, the solution as well as the ignited salt absorbing moisture from the air. The *disodic salt*, $Na^2HAsO^4 + 12H^2O$, separates from a solution of arsenic acid slightly supersaturated with carbonate of sodium, and left to evaporate below 18° C., in large efflorescent crystals isomorphous with ordinary phosphate of sodium. By leaving a more concentrated solution to crystallise at 20° C. or above, crystals are obtained belonging to the monoclinic system, containing 14 at. water, and not efflorescent. Both kinds of crystals give off the whole of their crystallisation-water, at 200° C., melt easily at a higher temperature, and give off their basic water, leaving the anhydrous salt, $2Na^2O.As^2O^5$, or $Na^4As^2O^7$; this anhydrous salt, however, recovers its basic water when redissolved. According to Setterberg, a salt with 26 at., water of crystallisation separates from a solution cooled to 0° C.

The *monosodic salt*, NaH^2AsO^4, is formed when arsenic acid is added to carbonate sodium till the solution no longer precipitates chloride of barium; it crystallises out after a while in the cold. It is more soluble than the disodic salt, and forms large crystals isomorphous with the corresponding phosphate.

Arsenate of Sodium and Ammonium, $Na(NH^4)HAsO^4 + 4H^2O$, is obtained by mixing the solutions of the di-ammonic and disodic salts, in crystals exactly resembling those of the corresponding phosphate (microcosmic salt). When heated to redness, they leave monosodic arsenate. (Mitscherlich.)

Arsenate of Sodium and Potassium, $KNaHAsO^4 + 16H^2O$. (Mitscherlich).—Obtained by neutralising the monosodic salt with carbonate of potassium. The crystals contain, according to Mitscherlich's analysis, 43·88 per cent. water, the preceding formula requiring 44·16 per cent.; but as they appear to be ismorphous with the disodic salt containing 14 at., L. Gmelin (Handbook iv. 299) considers it probable that they also contain the same quantity of water.

Arseno-fluoride of Sodium, $Na^3AsO^4.NaF + 12H^2O$.—Prepared by gradually introducing a mixture of 1 pt. arsenious oxide, 4 pts. carbonate of sodium, 3 pts. nitrate of sodium, and 1 pt. fluor-spar, into a red-hot crucible, and ultimately heating to complete fusion. On boiling the fused mass with water and filtering, the double salt crystallises out in regular octahedrons, exactly like common alum. They have a specific gravity of 2·849 at 21° C., dissolve in 9·5 pts of water, at 25° C., and in 2 pts. at 75° C. (Briegleb, Ann. Ch. Pharm. xcvii. 95.)

Arsenosulphate of Sodium.—A solution of 3 at. Na^2HAsO^4, mixed with 1 at. sulphuric acid, yields crystals containing $Na^8As^6O^{19}.2Na^2SO^4$, or $4Na^2O.3As^2O^5 + 2(Na^2O.SO^3)$; their solution slightly reddens litmus, but still turns turmeric brown (Mitscherlich). By dissolving sulphate of sodium and disodic arsenate together in equivalent proportions, or by heating anhydrous disodic arsenate in a current of sulphurous anhydride (half the arsenic acid being then reduced to arsenious acid, which volatilises), and subsequent recrystallisation, a salt is obtained, composed of $Na^2SO^4.Na^4As^2O^7$, which does not alter by exposure to the air, and fuses more easily than either of its component salts. (Setterberg.)

Arsenate of Strontium, Sr^2HAsO^4.—Resembles the barium-salt. By precipitating its solution in nitric acid with excess of ammonia, a double salt is produced containing $Sr(NH^4)AsO^4 + \frac{1}{2}H^2O$.

Arsenate of Thorinum, is obtained by double decomposition, as a white flocculent precipitate, insoluble in water and in the aqueous acid.

Arsenate of Titanium.—Arsenic acid added to solution of titanic oxide, throws down white flocks, which dry up to vitreous masses, and are soluble in free titanic acid, as well as in arsenic acid.

Arsenates of Tin.—The *stannic* salt, $2SnO^2.As^2O^5 + 10H^2O$, or $(\overset{''}{Sn})^2As^2O^8.10H^2O$, is precipitated as a gelatinous mass when a mixed solution of stannate and excess of arsenate of sodium is treated with excess of nitric acid. It is transparent when dry, and gives off all its water at 120° C. (Haeffely, Phil. Mag. [4] x. 290.)

Stannous Arsenate is a white precipitate obtained by adding arsenic acid to stannous chloride or acetate. Tin heated with aqueous arsenic acid eliminates hydrogen and forms a gelatinous mass.

Arsenates of Uranium.—*Uranic arsenate*, or *Arsenate of Uranyl*, $(U^2O)^2HAsO^4 + 4H^2O$, is formed by precipitating uranic acetate with arsenic acid, or uranic nitrate with arsenate of sodium. It is a yellow precipitate which gives off its water at 120° C.

A *sodio-uranic nitrate*, $(U^2O)NaAsO + \frac{5}{2}H^2O$, is obtained by mixing a solution of uranic nitrate with trisodic arsenate; and by boiling uranic arsenate with solution of basic acetate of copper (obtained by digesting verdigris with water), a green *cupro-uranic arsenate* is formed, containing $(U^2O).CuAsO^4 + 4Aq$. (Werther.)

Uranous Arsenate, $U^2HAsO^4 + \frac{3}{2}H^2O$, is a green precipitate obtained by treating uranous chloride with disodic arsenate. It dissolves in hydrochloric acid, and the solution mixed with excess of ammonia yields a very bulky precipitate of *tri-uranous arsenate*, U^3AsO^4. (Rammelsberg, Pogg. Ann. lix. 96.)

Arsenates of Vanadium.—A solution of vanadic hydrate in excess of arsenic acid yields by evaporation, a crust of blue crystalline granules, containing 1 at. vanadic oxide (VO) to 1 at. anhydrous arsenic acid. It dissolves very slowly in water, but easily in hydrochloric acid. A more basic salt is obtained as a syrupy mass, mixed with crystals of the preceding salt, by evaporating a solution of arsenic acid saturated with vanadic oxide.

If the solution of the crystalline compound in nitric acid be evaporated till nitrous acid begins to escape, a yellow powder is deposited, which is a compound of vanadic and arsenic anhydrides, $2V^2O^5.3As^2O^5$.

Arsenate of Yttrium.—The *di-yttric* salt obtained by precipitation is a white heavy powder, which dissolves in nitric acid, and separates therefrom in crystalline grains. The nitric acid solution supersaturated with ammonia yields the *tri-yttric* salt. Yttria dissolves in excess of arsenic acid, but the solution when heated deposits the di-yttric salt.

Arsenate of Zinc.—Acetate of zinc treated with arsenic acid or arsenate of sodium, yields a white precipitate, which dissolves in excess of arsenic acid, and separates on evaporation in cubical crystals of an acid salt. Zinc dissolves in aqueous arsenic acid, with evolution of arsenetted hydrogen, and deposition of metallic arsenic mixed with brown solid arsenide of hydrogen. When zinc and arsenic oxide are fused together, a large quantity of arsenic is reduced, with slight detonation.

Trizincic Arsenate, $Zn^3AsO^4 + 4H^2O$, occurs as *Köttigite* in the Daniel cobalt mine near Schneeberg in Saxony, forming monoclinic crystals, or crusts with crystalline structure. Specific gravity 3·1. Hardness 2·5—3. It is of light carmine or peach-blossom colour, translucent, and gives a reddish-white streak. The zinc is partly replaced by cobalt and nickel. Analysis 37·2 per cent. As^2O^5, 30·5 Zn^2O, 6·9 Co^2O, 2·00 Ni^2O, with trace of lime, and 23·4 water. (Köttig, J. pr. Chem. xlvii. 183; Naumann, *ibid.* 256.)

Sulphate of zinc added to a solution of arsenate of sodium containing ammonia produces a precipitate of trizincic arsenate, which soon changes to a crystalline compound containing, according to Bette, $Zn^3AsO^4.NH^3.\frac{3}{2}H^2O$ (?)

Arsenate of Zirconium.—White precipitate insoluble in water.

ARSENIC, OXYBROMIDE OF. *Bromarsenious Acid.* AsBrO.—Arsenious oxide dissolves easily and abundantly in fused arsenious bromide, forming a somewhat viscid dark-coloured liquid, which does not solidify so quickly as the pure bromide. If this liquid be distilled till it becomes rather thick and then allowed to cool to about 150° (C. or F.?) it separates into two layers, the lower of which is a soft dark-coloured mass, consisting of the oxybromide AsBrO, while the upper, which is very viscid, is a compound of the oxybromide with arsenious oxide, probably $6AsBrO.As^2O^3$; both these bodies are decomposed by heat, giving off bromide of arsenic (W. Wallace, Phil. Mag. [4] xvii. 122). An oxybromide of arsenic is likewise formed by the action of water on the bromide (Serullas). When bromide of arsenic is boiled with a quantity of water containing hydrobromic acid not sufficient to dissolve it, the undissolved portion is converted into oxybromide. A cold solution of bromide of arsenic in water containing hydrobromic acid, yields, by evaporation over sulphuric acid, thin white pearly crystals, consisting of hydrated oxybromide, $2AsBrO.3H^2O$. A solution of bromide of arsenic in water, prepared at the boiling heat, deposits on cooling crystals of arsenious oxide; but if the water contains a large quantity of hydrobromic acid, the solution deposits on cooling ,white flocks of a compound, which after drying between filter-paper, consists of $2AsBrO.3As^2O^3 + 12H^2O$.—When bromide of ammonium is added to a cold concentrated solution of bromide of arsenic, six-sided tables are slowly deposited, consisting mainly of anhydrous bromide of arsenic. (Wallace, *loc. cit.*)

ARSENIC, OXYCHLORIDE OF. *Chlorarsenious Acid.* $AsClO$, or $AsCl^3.As^2O^3$. —Pulverised arsenious oxide added in successive portions to boiling chloride of arsenic continues to dissolve till the liquid contains 2 at. chloride to 1 at. oxide. The same solution is obtained by passing dry hydrochloric acid gas into a vessel containing dry arsenious oxide till the latter is dissolved: great heat is evolved during the reaction. On distilling the solution obtained by either process, till it begins to froth, and leaving the residue to cool, oxychloride of arsenic separates as a viscid, translucent, brownish mass, which fumes slightly in the air, and absorbs oxygen from it, froths when strongly heated, giving off chloride of arsenic, and at the subliming temperature of arsenious oxide, leaves a hard vitreous residue, consisting of $AsClO.As^2O^3$.

Oxychloride of arsenic is likewise produced when chloride of arsenic is treated with a quantity of water not sufficient to dissolve it completely. A solution of chloride of arsenic in the smallest possible quantity of water ($8H^2O$ to $1AsCl^3$) deposits, after some days, small, white, needle-shaped crystals, grouped in stars or like prehnite, and consisting of $AsClO.H^2O$; the mother-liquor yields an additional quantity when mixed with chloride of sodium.

Oxychloride of arsenic unites with metallic chlorides. By mixing aqueous chloride of arsenic with a quantity of hydrochloric acid sufficient to prevent the separation of oxychloride, and then adding a lump of sal-ammoniac, crystals of that salt separate out at first, and after a few days, fibrous needles of the compound $AsClO.2NH^4Cl$, apparently containing ½ at. H^2O, which is given off when the crystals are left over sulphuric acid. (Wallace Phil. Mag. [4] xvi. 358.)

ARSENIC, OXYIODIDE OF. $As^8I^2O^{11} = 2AsIO.3As^2O^3$.—A hot aqueous solution of arsenious iodide deposits, when concentrated by boiling, fine red needles of the anhydrous iodide; but if left to cool slowly, it deposits thin pearly laminæ, which after drying between bibulous paper, are composed of $2AsIO.3As^2O^3 + 6H^2O$, and give off all their water over sulphuric acid. They are decomposed by water, and when heated yield a sublimate chiefly consisting of iodide of arsenic, while arsenious oxide remains behind (Wallace, Phil. Mag. [4] xvii. 122). The formation of this compound had previously been observed by Plisson and by Serullas and Hottot, who regarded it as a compound of arsenious oxide with arsenious iodide. (Gm. iv. 282.)

ARSENIC, OXYSULPHIDE OF. See SULPHOXARSENATE OF POTASSIUM (p. 395).

ARSENIC, SULPHIDES OF. The sulphides of arsenic are more numerous than the oxides. There are three well defined sulphides, AsS, As^2S^3, and As^2S^5 [or AsS^2, AsS^3, and AsS^5, if $S = 16$], all of which act as sulphur-acids. The first two occur as natural minerals, *realgar* and *orpiment*, and may also be obtained in the free state by artificial processes; the third is known only in combination. Besides these compounds, there is a *subsulphide*, $As^{12}S$ (?), which remains as a brown powder when the disulphide AsS is digested with caustic alkalis; and, according to Berzelius, a *persulphide*, AsS^9, obtained in yellow crystalline scales, by mixing a solution of dipotassic or disodic sulpharsenate with alcohol, and evaporating to about two-thirds; but the product thus obtained is most probably a sulpharsenate with excess of sulphur. When arsenious oxide is fused with sulphur, sulphurous anhydride is evolved, and a sulphide of arsenic containing excess of sulphur remains. On distilling this residue, sulphur passes over, accompanied by a continually increasing quantity of arsenic. Much of the ordinary sulphur of commerce is a compound of this nature.

DISULPHIDE OF ARSENIC. AsS. *Realgar, Red Orpiment,* or *Ruby Sulphur; rothes Rauschgelb, Arsenic sulphuré rouge, Risigallo; Sandaraca* of Pliny and Vitruvius; σανδαρακη of Theophrastus and Dioscorides. In combination: HYPOSULPHARSENIOUS ACID.—This compound occurs native as realgar, crystallised in oblique rhombic prisms of the monoclinic system, having an orange-yellow or aurora-red colour, resinous lustre, and more or less translucent: streak varying from orange-red to aurora-red; fracture conchoïdal, uneven; sectile. Specific gravity = 3·4 to 3·6.

Hardness = 1·5 to 2. It is found accompanying ores of silver and lead, at Andreasburg in the Harz, Kapnik and Nagyag in Transylvania, Felsöbanya in Hungary, Joachimsthal in Bohemia, and Schneeberg in Saxony. At Tajowa in Hungary, it occurs in beds of clay; at St. Gothard imbedded in dolomite; near Julamerk in Koordistan; also in the Vesuvian lavas, in minute crystals. Strabo speaks of a mine of *sandaraca* at Pompeiopolis, in Paphlagonia. (Dana.)

Disulphide of arsenic may be prepared by melting metallic arsenic with sulphur or orpiment, or sulphur with arsenious oxide, in the required proportions. As thus obtained, it is transparent and of a ruby-colour, easily fusible, and crystalline after solidification from fusion. An impure product is prepared on the large scale by heating in a subliming apparatus a mixture of arsenical pyrites and iron-pyrites, and melting the product with arsenic or sulphur, according as a darker or lighter colour is desired. This commercial product is amorphous, usually brown-red, opaque, and of variable composition, generally containing arsenious oxide. It is used as a pigment, though not so much now as formerly.

Disulphide of arsenic burns in the air with a blue flame, forming sulphurous and arsenious oxides. When deflagrated with nitre, it produces a bright white light. *Indian white fire* is a mixture of 24 pts. nitre, 7 pts. sulphur, and 2 pts. realgar. The disulphide heated with nitric acid, yields arsenic acid and free sulpur. With strong *sulphuric acid*, it forms sulphurous and arsenious acids. When it is digested in fine powder with *potash-ley*, part dissolves and there remains a brown powder consisting of $As^{12}S$. (?)

HYPOSULPHARSENITES.—These are sulphur-salts formed by the mixing of disulphide of arsenic with basic sulphides. They are for the most part sparingly soluble in water. The little that is known of them is due to the researches of Berzelius.

The *ammonium-salt* is deposited in small dark brown granules on the sides of a closed vessel in which neutral sulpharsenite of ammonium is kept for a long time. It absorbs ammonia-gas, but gives it off again on exposure to the air.

Hyposulpharsenite of Potassium.—The colourless liquid obtained by boiling trisulphide of arsenic with moderate concentrated carbonate of potassium, deposits in the course of 12 hours, brown-red flocks of the salt $K^2S.AsS$, or K^2AsS^2. If this compound be washed with a small quantity of cold water till it swells up to a jelly, and then treated with more water, the greater part dissolves, forming a red solution of the salt, $3K^2S.2AsS$, and leaving an insoluble dark-brown powder consisting of $K^2S.4AsS$, which melts easily when heated, and solidifies on cooling to a transparent dark red mass. The basic salt $3K^2S.2AsS$, remains perfectly soluble in water, even after complete drying.

The *sodium hyposulpharsenites* resemble those of potassium.

Other hyposulpharsenites are obtained by precipitation. The *barium* and *calcium salts* are red-brown; the *magnesium-salt* is brown; the *manganese-salt* dark red.

TRISULPHIDE OF ARSENIC, or ARSENIOUS SULPHIDE. In combination: SULPHARSENIOUS ACID. **As^2S^3, or AsS^3.** *Orpiment, Yellow Sulphide of Arsenic, Gelbes Rauschgelb, Risigallum, Auripigmentum* (Vitruvius); *Arsenicum* (Pliny); **'Αρσένικον** (Dioscorides); **'Αῤῥένικον** (Theophrastus).—This sulphide occurs native in rhombic prisms belonging to the trimetric system, easily splitting parallel to ∞P∞ into thin flexible laminæ. They are translucent, of lemon-yellow colour, inclining to orange-yellow, with pearly lustre on the cleavage-faces, resinous elsewhere; powder lemon-yellow; specific gravity 3·459 (Karsten), 3·48 (Mohs, Haidinger), 3·4 (Breithaupt).

Trisulphide of arsenic is obtained in the pure state by passing hydrosulphuric acid gas into a solution of arsenious acid or an arsenite acidulated with one of the stronger acids. As thus prepared, it has a fine lemon-yellow colour, becoming darker by heat, and produces an orange-yellow powder: it melts easily and volatilises at a higher temperature.

An impure trisulphide is prepared on the large scale by subliming 7 parts of pulverised arsenious oxide with 1 pt. of sulphur. It always contains more or less oxide, inasmuch as to convert that compound completely into trisulphide requires 7·3 pts. of sulphur to 10 pts. of the oxide: hence this preparation is much more poisonous than the pure artificial sulphide or the native sulphide. It was formerly much used as a pigment, under the name of *King's yellow*, but is now almost entirely superseded by chrome-yellow. The arsenious oxide may be extracted from it by boiling with water, or with dilute aqueous acids, or cream of tartar.

Arsenious sulphide is also used in calico printing, the pattern being printed with a preparation containing arsenious acid, and then passed through water containing hydrosulphuric acid. A solution of orpiment in potash-ley is used in dyeing as a deoxidising agent, especially for reducing indigo. A paste composed of slaked lime, orpiment, and water, is employed by some nations as a depilatory for removing the beard; but it is a dangerous preparation, and, according to Böttger may be replaced for this purpose by sulphydrate of calcium.

Decompositions.—1. Arsenious sulphide, like all the other sulphides of arsenic, is converted by *oxidising agents* into oxides of sulphur and arsenic. When it is fused with *acid sulphate of potassium*, sulphurous oxide (SO^2) is given off, and arsenite of potassium remains mixed with neutral sulphate.—2. Exposed to the action of *chlorine gas*, it becomes heated, and deliquesces to a brown liquid consisting of a sulphochloride of arsenic, $As^2Cl^6S^3$ (H. Rose).—3. The vapour of arsenious sulphide passed over red-hot *iron*, *silver*, and other metals, is decomposed, yielding a metallic sulphide and free arsenic, which, if the other metal is in excess, unites with it.

4. When the vapour is passed over red-hot lime, arsenic is separated, and arsenate of calcium is produced, together with sulphide of calcium.

5. Arsenious sulphide heated with *carbonate of potassium* or *sodium* in a glass tube, yields a mirror of arsenic, together with sulpharsenate and arsenate of the alkali-metal. If the mixture is heated in an atmosphere of *hydrogen*, or with addition of *charcoal*, the arsenical mirror is increased by the arsenic reduced from the arsenate; the sulpharsenate remains undecomposed. (H. Rose, Pogg. Ann. xc. 565.)

6. When arsenious sulphide is heated in a test-tube with a mixture of *alkaline carbonate* and *cyanide of potassium*, the whole of the arsenic is reduced, according to Fresenius; only part of it, according to H. Rose, because the sulphur-salt of arsenic formed at the same time resists the action of the cyanide of potassium. Hence arsenious sulphide fused with cyanide of potassium and excess of sulphur does not yield any arsenical mirror. The formation of the mirror may also be prevented by the presence of other easily reducible metals, which convert the arsenic into an arsenide, and do not give it up.

7. When arsenious sulphide is boiled with the solution of an *alkaline carbonate*, and the concentrated solution is filtered, a clear liquid is obtained, which deposits a brown powder, consisting of hyposulpharsenite of the alkali-metal, while a sulpharsenate remains in solution. A similar decomposition takes place when a soluble neutral sulpharsenite is treated with water.

8. Arsenious sulphide is readily dissolved by cold caustic potash, soda, or ammonia, undergoing exactly the same decomposition as antimonious sulphide under similar circumstances (p. 322), the oxygen of the alkali converting the arsenic into arsenious acid, while the alkali-metal unites with the sulphur, and the basic sulphide thus formed combines with the rest of the arsenious sulphide:

$$4As^2S^3 + 5K^2O = 3(K^2S.As^2S^3) + 2K^2O.As^2O^3$$

On adding an acid to this solution, no sulphuretted hydrogen is evolved, but the whole of the sulphur and arsenic are separated as arsenious sulphide:

$$3(K^2S.As^2S^3) + 2K^2O.As^2O^3 + 10HCl = 10KCl + 5H^2O + 4As^2S^3$$

SULPHARSENITES.—Arsenious sulphide unites with basic metallic sulphides in three different proportions, forming, with potassium, for example, the compounds $3K^2S.As^2S^3$ or K^3AsS^3, $2K^2S.As^2S^3$ or $K^4As^2S^5$, and $K^2S.As^2S^3$ or $KAsS^2$ [or $3KS.2AsS^3$, $2KS.AsS^3$, and $KS.AsS^3$.—Of these, the *dibasic* or *tetrametallic* salts are the most common, and are regarded as neutral or normal sulpharsenites.

The soluble sulpharsenites are prepared: 1. By igniting sulpharsenates out of contact with the air, 2 at. sulphur then escaping.—2. by dissolving arsenious sulphide in an alkaline sulphide or sulphydrate; in the latter case, sulphuretted hydrogen is evolved.—3. By dissolving arsenious sulphide in a cold solution of caustic alkali.—4. By dissolving arsenious oxide in an alkaline sulphydrate, in which case half of the alkali is converted into arsenite; *e. g.*:

$$As^2O^3 + 2KHS = KAsS^2 + KAsO^2 + H^2O.$$

The only sulpharsenites that are soluble in water are those of the alkali-metals, alkaline earth-metals, and magnesium, and even these are decomposed by water, unless the water is in considerable quantity. Hence the solutions cannot be evaporated to dryness without decomposition. The solutions are colourless or yellowish, tasting hepatic at first, and afterwards disgustingly bitter.—5. The sulpharsenites of the earth-metals and heavy metals are obtained by precipitating a solution of the corresponding compound of an alkali-metal, obtained by either of the methods 2, 3, 4, with a salt of the earth-metal or heavy metal. (Berzelius.)

The sulpharsenites are either yellow or red. Most of them, when ignited out of contact of air, give off all their sulphur-acid; others give up such a quantity that the residue contains 3 at. sulphur-base to 1 at. sulphur-acid; but the sulpharsenites of the alkali-metals, even those which contain equal numbers of atoms of base and acid, give off nothing when ignited. The alkali-metal compounds obtained by the first method, when treated with a small quantity of water, and the dilute solutions obtained by method 2, 3, or 4, when they evaporate in the air, are resolved into brown hyposulpharsenite which is precipitated, and sulpharsenate which remains in solution; but the decomposition is not complete till the solution is concentrated to the crystallising point of the latter salt. If the decomposed mass be digested in a large quantity of water and boiled, the whole is reconverted into sulpharsenite and redissolved. The solutions of the barium, strontium, calcium, and magnesium salts, containing 1 at. base to 1 at. acid, deposit, on boiling, a portion of the arsenious sulphide; the ammonium, potassium, sodium, and lithium compounds remain undecomposed. On adding alcohol to the aqueous solution of a compound of 1 at. of arsenious sulphide with 2 at. of the sulphide of an alkali-metal, a compound containing 3 at. of sulphur-base is precipitated, while a compound containing 1 at. of sulphur-base remains in solution:

$$2(2K^2S.AsS^3) = 3K^2S.AsS^3 + K^2S.AsS^2.$$

But the precipitated tribasic salt soon turns black, being resolved into hyposulpharsenite and sulpharsenate. The potassium and sodium compounds exhibit this blackening on the addition of alcohol, even when the solution contains nothing but tribasic salt ($3K^2S.As^2S^3$); but with the ammonium, barium, strontium, and calcium salts, it does not take place unless the solution contains dibasic salt ($2Ba^2S.As^2S^3$). — Aqueous solutions of sulpharsenites exposed to the air are decomposed by oxidation (more slowly in proportion to the excess of sulphur-base), depositing orpiment and a brown compound of disulphide of arsenic with the sulphur-base. Hydrated oxide of copper, added to a solution containing a compound of sulpharsenious acid with the sulphide of an alkali-metal, decomposes that compound, yielding twelve-basic sulpharsenite of copper, which remains undissolved, and a hyacinth-red solution, containing an alkaline arsenite and tribasic sulpharsenite of copper, and deposits the latter on the addition of hydrochloric acid. Perhaps in this manner:

$$9(K^2S.As^2S^3) + 27Cu^2O = 2(12Cu^2S.As^2S^3) + 3Cu^2S.As^2S^3 + 3(3K^2O.2As^2O^3).$$

If the hydrated oxide of copper is in excess, the arsenious acid contained in the solution is converted into arsenic acid, and the protoxide of copper reduced to sub-oxide. — Oxide of silver in excess decomposes the solution, forming sulphide of silver and alkaline arsenite:

$$KAsS^2 + 2Ag^2O = 2Ag^2S + KAsO^2.$$

Sulpharsenite of Ammonium, $2(NH^4)^2S.As^2S^3$. — The solution of arsenious sulphide in sulphide of ammonium or caustic ammonia yields, when mixed with alcohol, a precipitate of this composition, which, however, soon turns brown. If previously mixed with sulphydrate of ammonium, it deposits white feathery crystals of the basic salt $(3NH^4)^2S.As^2S^3$. Finely divided arsenious sulphide absorbs 6½ per cent. of ammonia-gas, but gives it up again when exposed to the air.

Sulpharsenite of Barium.—The solution of arsenious sulphide in sulphydrate of barium dries up to a red-brown gummy mass of the neutral salt, $2Ba^2S.As^2S^3$, perfectly soluble in water. Alcohol precipitates from the solution crystalline flakes of the basic salt, $3Ba^2S.As^2S^3$, which is likewise obtained by treating arsenious sulphide with excess of sulphide of barium.

Sulpharsenite of Bismuth, $2Bi^2S^3.As^2S^3$, is a red-brown precipitate, which turns black in drying. By fusion, a grey metallic-shining mass is obtained, consisting of the basic salt.

Sulpharsenite of Cadmium.—Cadmium-salts mixed with a saturated solution of arsenious sulphide in sulphide of ammonium, yield a yellow precipitate, $2Cd^2S.As^2S^3$. which becomes orange-yellow when dry, and semifluid when heated, giving off part of the arsenious sulphide, and leaving a fused grey compound containing a larger proportion of cadmic sulphide.

Sulpharsenite of Calcium.—When orpiment is digested with milk of lime, and the solution is filtered from the arsenite of calcium, which forms at the same time, a colourless filtrate is obtained, which, by spontaneous evaporation, yields feathery crystals of the basic salt $3Ca^2S.As^2S^3$, surrounded by a brown syrup of the neutral salt $2Ca^2S.As^2S^3$. This syrup digested with an additional quantity of arsenious sulphide turns yellow and deposits a brown powder consisting of *hyposulpharsenite* of calcium, $Ca^2S.2AsS$. The solution of the sulpharsenite containing excess of sulphide of calcium yields, with alcohol, a white precipitate of the basic salt, containing $3Ca^2S.As^2S^3 + 15Aq$.

Sulpharsenite of Cerium, $2Ce^2S.As^2S^3$.—Yellow precipitate, which acquires a deeper colour when dry, melts, and evolves part of the arsenious sulphide when heated, and when roasted gives up all its arsenic, and is completely converted into sulphate.

Sulpharsenite of Chromium, $2Cr^4S^3.3As^2S^3$. — Greyish-yellow precipitate, greenish-yellow after drying. When heated, it melts and gives off part of the arsenious sulphide, and is converted into chromic oxide by roasting.

Sulpharsenite of Cobalt, $2Co^2S.As^2S^3$, is a dark brown precipitate, which becomes black in drying, dissolves in excess of the precipitant, and when ignited in close vessels, leaves a residue having the composition of cobalt-glance.

Sulpharsenite of Copper.—A twelve-basic salt, $12Cu^2S.As^2S^3$, remains undissolved as a brown mass, when cupric hydrate is added to solution of monopotassic sulpharsenate, till the colour of the liquid is no longer altered. The *tribasic salt*, $3Cu^2S.As^2S^3$, is precipitated in light brown flakes on adding hydrochloric acid to the hyacinth-red solution obtained in the manner just mentioned. The neutral salt, $2Cu^2S.As^2S$, is obtained by adding neutral sulpharsenite of sodium to a cupric salt, as a black-brown precipitate, which acquires a metal-grey aspect by trituration. When distilled, it first gives off sulphur, then arsenious sulphide, and leaves a tumefied metal-grey substance, probably consisting of cuprous hyposulpharsenite.

Sulpharsenite of Glucinum, $2G^2S.As^2S^3$, is a yellow precipitate, formed, without evolution of sulphuretted hydrogen, on adding a neutral glucinum-salt to a solution of sulphide of sodium saturated with arsenious sulphide. Acids separate but little sulphuretted hydrogen from it, ammonia partly dissolves it, and leaves pure glucina.

Sulpharsenite of Gold, $2Au^2S^3.3As^2S^3$.—Yellow precipitate, becoming darker as it settles down, black when dry, and yielding by trituration a yellow-brown powder. At a dull red heat, it melts, gives off part of the arsenious sulphide, and solidifies to a transparent yellow-red mass, yielding by dry trituration a yellow-brown mass, which, however, by continued trituration under water, assumes a metallic lustre, as if from reduced gold. To expel the whole of the arsenious sulphide requires a full white heat.

Sulpharsenites of Iron.—The *ferric salt*, $2Fe^4S^3.3As^2S^3$, is an olive-green precipitate, soluble in excess of the precipitating alkaline sulpharsenite, acquiring a green colour when dry, and a fine yellow-green by trituration. It melts easily when heated, and decomposes at a red heat, leaving pure sulphide of iron. The *ferrous salt*, $2Fe^2S.As^2S^3$, is a brown-black precipitate, also soluble in excess of the precipitant; grey-brown when dry, dark greenish after trituration. It is decomposed by heat, leaving pure sulphide of iron. The dried precipitate always contains ferric oxide mixed with the preceding salt.

Sulpharsenite of Lead, $2Pb^2S.As^2S^3$.—Red-brown precipitate, black when dry; melts to a brittle metallic-looking mass, a shining grey crystalline fracture, and yielding a grey powder.

Sulpharsenite of Lithium resembles the potassium- and sodium-salts.

Sulpharsenite of Magnesium.—The aqueous solution evaporated, or cooled to −5° C., becomes light brown, and deposits a brown powder consisting of hyposulpharsenite of magnesium; then dries to a viscid mass, which ultimately solidifies, and is almost wholly soluble in water.

Sulpharsenite of Manganese.—Light red precipitate, becoming orange-yellow when dry. Heated in close vessels, it gives off a considerable portion of the arsenious sulphide, and leaves a yellow-green compound, from which hydrochloric acid extracts the manganese, with evolution of sulphuretted hydrogen, leaving a residue of arsenious sulphide.

Sulpharsenites of Mercury.—The neutral *mercuric salt*, $2Hg^2S.As^2S^3$, is an orange-red flocculent precipitate, which becomes white in presence of excess of mercuric chloride, but retains its colour if the precipitant is in excess. It is dark brown when dry, and gives a yellow powder. When heated, it yields a grey metallic-shining sublimate of $Hg^2S.As^2S^3$, which is translucent in thin films, and yields a yellow powder when finely ground. The *mercurous salt*, $2Hg^4S.As^2S^3$, is a black precipitate, which decrepitates with explosion when distilled, giving off mercury and yielding a sublimate of mercurous hyposulpharsenite in black opaque metallic crusts, which yield a red powder.

Sulpharsenite of Molybdenum.—The solution of molybdic acid in hydrochloric acid forms with sulpharsenite of sodium, a dark brown powder, which becomes black in drying, and decomposes at a red heat, giving off arsenious sulphide and sulphur, and leaving disulphide of molybdenum, MoS.

Sulpharsenite of Nickel, $2Ni^2S.AsS^3$, is a black precipitate, which, when distilled, easily gives off all its arsenious sulphide, and leaves yellow sintered sulphide of nickel.

Sulpharsenite of Potassium.—The neutral salt, $2K^2S.As^2S^3$, is obtained by igniting the corresponding sulpharsenate ($2K^2S.As^2S^5$) till the excess of sulphur is driven off. It is a dark yellow mass, which becomes yellow on cooling. Treated with water, it yields a solution of basic sulpharsenate ($3K^2S.As^2S^3$) and a residue of hyposulpharsenite. When arsenious sulphide is dissolved at mean temperature in aqueous sulphydrate of potassium, till all the sulphuretted hydrogen is eliminated, the solution contains an *acid sulpharsenite*, $K^2S.2As^2S^3$. This solution is decomposed by evaporation, depositing brown hyposulpharsenite of potassium, $K^2S.AsS$. On mixing the solution with alcohol, a white precipitate of $3K^2S.As^2S^3$ is formed at first; but it soon becomes brown and syrupy, and deposits the hyposulpharsenite. When carbonate of potassium is fused with arsenious sulphide till the excess of the latter is expelled, there remains a mass, consisting of $K^2S.As^2S^3$. This salt is decomposed by water, the acid salt, $K^2S.2As^2S^3$, dissolving, and a compound, still richer in arsenious sulphide, remaining undissolved.

Sulpharsenite of Silver, $2Ag^2S.As^2S^3$, is a light brown precipitate, transparent at first, becoming black during collection; when heated in the dry state, it melts and gives off part of the arsenious sulphide. The black fused mass yields a brown powder. When acid sulpharsenite of sodium is precipitated by a saturated solution of chloride of silver in ammonia, a dark yellow precipitate is formed, containing $6Ag^2S.As^2S^3$.

Sulpharsenite of Sodium.—Strictly analogous to the potassium-salt.

Sulpharsenites of Tin.—The *stannous salt*, $2SnS.As^2S^3$, is a dark red-brown precipitate, infusible, but giving off part of its sulphur at high temperatures. The *stannic salt*, $SnS^2.As^2S^3$, is a gummy yellow precipitate, which becomes orange-yellow when dry.

Uranic Sulpharsenite, $2U^4S^3.As^2S^3$, is a dingy yellow precipitate, which melts and gives off part of its sulphur when heated, and, after exposure to a white heat, leaves a grey porous mass, still containing arsenious sulphide.

Sulpharsenite of Zinc, $2Zn^2S.As^2S^3$.—Lemon-yellow precipitate, orange-yellow when dry; gives off arsenious sulphide when heated, leaving a more basic compound, and at a higher temperature, pure sulphide of zinc.

Sulpharsenite of Zirconium, $2Zr^4S^3.As^2S^3$.—Orange-yellow precipitate, quite insoluble in excess of the alkaline sulpharsenite.

PENTASULPHIDE OF ARSENIC, OR ARSENIC SULPHIDE. In combination: SULPHARSENIC ACID. As^2S^5, or *AsS*^{5}.—A substance containing arsenic and sulphur in this proportion is precipitated when a soluble sulpharsenate is decomposed by hydrochloric acid; but it appears to be rather a mixture of the trisulphide with free sulphur. When sulphuretted hydrogen is passed into an aqueous solution of arsenic acid, sulphur is first separated, and remains for a long time suspended in the liquid. The precipitate contains a very small quantity of trisulphide of arsenic, which may be extracted by dilute ammonia, pure sulphur then remaining. The filtered liquid is then found to contain arsenic acid, together with a small quantity of arsenious acid; and, if sulphuretted hydrogen be then rapidly passed through it for a short time, a precipitate of trisulphide of arsenic is obtained. If this precipitate be separated by filtration, and the passage of the sulphuretted hydrogen continued, the liquid again becomes turbid from separation of sulphur, and, by repeating these operations, the whole of the arsenic may be precipitated as trisulphide. (H. Rose, Pogg. Ann. cvii. 186; H. Ludwig, Arch. Pharm. [2] xcvii. 23.)

A sulphide of arsenic corresponding to anhydrous arsenic acid, As^2O^5, does not therefore appear to exist in the free state. Nevertheless, the precipitate thrown down by acids from solutions of sulpharsenates has the composition of the pentasulphide, and as such dissolves completely in alkaline sulphides and in strong ammonia; dilute ammonia, however, dissolves out the trisulphide and leaves the sulphur.

SULPHARSENATES.—These salts may be regarded as compounds of pentasulphide of arsenic with basic metallic sulphides. Our knowledge respecting them is chiefly due to the researches of Berzelius. They are for the most part *mono-*, *di*, or *tribasic*, a few instances only occurring of sulpharsenates with larger proportion either of sulphur-base or sulphur-acid. Their general formulæ are:

Monobasic or Monometallic .	$M^2S.As^2S^5$ or $MAsS^3$	$= \left.\begin{matrix}\overset{\prime}{As}S^2\\ M\end{matrix}\right\\}S$ *
Dibasic or Tetrametallic .	$2M^2S.As^2S^5$ or $M^4As^2S^7$	$= \left.\begin{matrix}\overset{\prime\prime\prime}{As^2}S^3\\ M^4\end{matrix}\right\\}S^4$
Tribasic or Trimetallic .	$3M^2S.As^2S^5$ or M^3AsS^4	$= \left.\begin{matrix}\overset{\prime\prime}{As}S\\ M^3\end{matrix}\right\\}S^3$

* Or $MS.AsS^5$, $2MS.AsS^5$, and $3MS.AsS^5$.

The tetrametallic salts are generally regarded as neutral; the monometallic as acid; the trimetallic as basic.

The sulpharsenates are prepared: 1. By passing sulphuretted hydrogen through the solution of an arsenate in water or in hydrochloric acid, thus:

$$K^3AsO^4 + 4H^2S = K^3AsS^4 + 4H^2O.$$

—2. By fusing orpiment with excess of sulphur and a caustic alkali or alkaline carbonate. —3. By digesting the trisulphide in an aqueous solution of a disulphide or polysulphide of alkali-metal.—4. By dissolving the pentasulphide ($As^2S^3 + 2S$) in a caustic alkali, or in an alkaline carbonate at the boiling heat. In this case an arsenate is formed at the same time.—5. Those sulpharsenates which are insoluble in water may be obtained by precipitation from the solution of an alkaline sulpharsenate.

The dry sulpharsenates of the alkali-metals are lemon-yellow; the others red or brown. They are permanent in the air. Those which are soluble taste hepatic at first, afterwards intensely bitter. The tribasic salts have a tendency to crystallise; the dibasic and monobasic salts are amorphous.

The trimetallic sulpharsenates of potassium, sodium, lithium, and barium may, if air be excluded, be heated almost to whiteness without decomposition; on cooling, they solidify to a yellow mass perfectly soluble in water. The tetrametallic and monometallic sulpharsenates of these metals give off sulphur when heated, and are converted into sulpharsenites. The silver- and mercury-salts (the latter of which sublimes) remain undecomposed at a red heat. The other tetrametallic and monometallic sulpharsenates are decomposed by ignition, first yielding sulphur and a red salt of sulpharsenious acid; and in many cases, the sulpharsenite is resolved by continued ignition into trisulphide of arsenic, which sublimes, and the sulphur-base, which remains behind. The calcium- and magnesium-salts first evolve sulphur, and then the greater part of the trisulphide, and leave a white unfused compound of magnesium- or calcium-sulphide, with a very small quantity of trisulphide; most of the heavy-metal-compounds evolve sulphur at first, and then all the sulphide of arsenic, so that nothing but the sulphur-base remains behind. The sulpharsenates, when heated in the air, give off orpiment and arsenious oxide, and leave a sulphate when the base contains an alkali-metal, and pure oxide if it contains a heavy metal. The aqueous solution of the sulpharsenate of an alkali-metal is decomposed by exposure to the air—the liquid becoming turbid, and depositing sulphur, pentasulphide of arsenic ($As^2S^3 + S^2$) and a brown salt of hyposulpharsenious acid, while alkaline arsenite and hyposulphite are formed, and the latter, by further oxidation, is converted into sulphate; the cooler and more concentrated the solution, the more slowly does the decomposition proceed. Acids, even carbonic acid, decompose the alkaline sulpharsenates, separating hydrosulphuric acid gas of a peculiar odour, and precipitating a mixture of arsenious sulphide and sulphur. Hydrated cupric oxide, introduced into the solution of an alkaline sulpharsenate, decomposes a portion of that compound, forming alkaline arsenate and sulphide of copper, a small portion of which dissolves in the liquid. A similar reaction is produced by other heavy metallic oxides which do not retain their oxygen with very great force. (Berzelius.)

Many sulpharsenates are soluble in water, namely, those of the alkali-metals, magnesium, yttrium, and glucinum. The solutions are either colourless or pale yellow. From the solutions of the dibasic salts alcohol precipitates a tribasic salt, and leaves monobasic salt in solution. When this solution is placed in a shallow dish, and evaporated at a gentle heat, there remains a lemon-yellow residue, from which water extracts a dibasic salt. (Berzelius.)

Sulpharsenate of Ammonium. $2(NH^4)^2S.As^2S^5 = (NH^4)^4As^2S^7$.—The solution of pentasulphide of arsenic in sulphide of ammonium, yields by evaporation, a viscid, reddish-yellow mass, which decomposes partially in drying, and still more when heated, first giving off a liquid containing disulphide of ammonium, and then yielding a sublimate of arsenious sulphide: $(NH^4)^4As^2S^7 = 4NH^4S + As^2S^3$.—The solution becomes brownish-yellow when boiled, and on cooling deposits a yellow powder composed of $(NH^4)^2S.12As^2S^5$. The aqueous solution of the dibasic salt is precipitated by alcohol, the *monammonic* or *acid* salt, NH^4AsS^3, then remaining in solution. If the solution be previously mixed with sulphide of ammonium and heated, alcohol throws down the *tri-ammonic* or *basic* salt $(NH^4)^3AsS^4$, in prismatic crystals.

Sulpharsenate of Antimony is a burnt-yellow, easily fusible precipitate.

Sulpharsenate of Barium.—The *tribarytic-salt*, Ba^3AsS^4, is obtained by decomposing the tetrabarytic or neutral salt: 1, by a red heat; 2, by mixing its aqueous solution with sulphide of barium, the mixture evaporated in vacuo over sulphuric acid at the freezing point, yielding the basic salt in loose, transparent, non-crystalline scales; 3, by precipitation with alcohol: it then falls down as a curdy precipitate, very soluble in water, probably a hydrate:—The *dibasic salt*, $Ba^4As^2S^7 = 2Ba^2S.As^2S^5$, is produced by saturating a solution of neutral arsenate of barium with hydrosulphuric acid. The solution dries up to a fissured lemon-yellow mass, which, if exposed to the air after all its water has been drawn off, absorbs water again, swelling up and falling to pieces at the same time. It dissolves in water in all proportions. With sulphate of potassium, it yields a precipitate of sulphate of barium, and a solution of neutral sulpharsenate of potassium.—The *monobarytic* or *acid* salt, $BaAsS^3$, remains in solution when the neutral salt is precipitated by alcohol. It is decomposed by evaporation, yielding a yellow deposit of the salt, $Ba^2S.3As^2S^3$, while the neutral salt remains in solution.

Sulpharsenate of Bismuth.—Both the basic and the neutral salts are dark-brown precipitates, soluble in excess of the alkaline sulpharsenate.

Sulpharsenate of Cadmium is a light yellow powder.

Sulpharsenate of Calcium.—The *basic salt*, Ca^3AsS^4, is obtained by mixing the solution of the neutral salt with sulphide of calcium, and either evaporating or precipitating with alcohol; it is not crystallisable, and when precipitated by alcohol, forms either a powder or a syrup, according to the quantity of water that it contains. It dissolves easily in water, but is insoluble in alcohol. The *neutral* salt, $Cu^4As^2S^7 = 2Ca^2S.As^2S^5$, is precisely analogous to the barium-salt. Its solution when evaporated, coagulates to a syrup, which, if then left to evaporate further, dries up to a yellow opaque mass, becoming anhydrous at 60° C.: when exposed to the air, it absorbs water, swells up, and detaches itself from the sides of the vessel. There appears to be no acid sulpharsenate of calcium.

Sulpharsenates of Cerium.—The *ceric salt*, $2Ce^4S^3.As^2S^3$, is a yellowish white precipitate, not quite insoluble in water, and consequently not appearing in very dilute solutions. The *cerous salts*, $Ce^2S.As^2S^5$, and $3Ce^2S.As^2S^5$, are obtained by double decomposition as precipitates of a fine yellow colour, which become somewhat darker when dry.

Sulpharsenate of Cobalt, $Co^4As^2S^7 = 2Co^2S.As^2S^5$, is a brown precipitate which becomes black when collected and dried, and dissolves with dark colour in excess of sulpharsenate of sodium.

Sulpharsenate of Copper, $Cu^4As^2S^7 = 2Cu^2S.As^2S^5$, is obtained as a dark brown precipitate, by treating solutions of copper-salts with neutral sulpharsenate of sodium, or by passing sulphuretted hydrogen through an acid solution containing arsenic acid and cupric oxide: if the arsenic acid is in excess, the brown sulphur-salt is first precipitated, and then yellow sulphide of arsenic. From a precipitate of this kind, sulphide of ammonium dissolves not only the sulphide of arsenic, but likewise by its intervention, a large portion of the sulphide of copper. Very dilute ammonia likewise extracts the sulphide of arsenic: stronger ammonia acquires a brown tint by taking up some of the sulphide of copper. (Gm. v. 475.)

Sulpharsenate of Glucinum.—Pentasulphide of arsenic digested with hydrate of glucinum and water, is dissolved to a small amount and reprecipitated by acids. Glucinum-salts are not precipitated by sulpharsenate of sodium.

Sulpharsenate of Gold.—The *tribasic salt*, $(\overset{\prime\prime\prime}{A}u)AsS^4 = (\overset{\prime\prime\prime}{A}u)^2S^3.As^2S^5$, is formed by precipitating a gold-solution with tribasic arsenate of sodium. It is a dark brown precipitate, soluble in pure water. Ferrous sulphate decolorises the solution, and throws a yellow-brown substance not yet examined. The *dibasic salt*, $2(\overset{\prime\prime\prime}{A}u)^2S^3.3As^2S^5$, obtained by precipitation with neutral sulpharsenate of sodium, dissolves in pure water, with brown red colour.

Sulpharsenates of Iron.—The *ferric* salt, $2Fe^4S^3.3As^2S^5$ = or $fe^4As^2S^7$, is a greyish-green precipitate, which dissolves with very dark colour in excess of the precipitant, is not altered by drying, but melts easily when heated, giving off sulphur, and being converted into ferric sulpharsenite.—The *ferrous salt*, $2Fe^2S.As^2S^5 = Fe^4As^2S^7$, is a dark brown precipitate, which dissolves in excess of the alkaline sulpharsenate. It decomposes in drying, assuming a rusty colour, and then consists of a mixture of the preceding salt with ferric oxide.

Sulpharsenate of Lead.—The salts Pb^3AsS^4, and $Pb^4As^2S^7$, are obtained by precipitation. The former is black-brown, the latter of a fine red colour; both turn black in drying.

Sulpharsenate of Lithium.—The *basic salt*, Li^3AsS^4, is precipitated by alcohol from the solution of the neutral salt in shining, colourless crystalline scales, soluble in hot water, and separating therefrom on cooling in six-sided prisms, and by spontaneous evaporation in four-sided tables with rhombic base. The *neutral* salt, $Li^4As^2S^7$, is a non-crystalline lemon-yellow mass, which absorbs moisture from the air, and is perfectly soluble in water. The *acid* salt, $LiAsS^3$, is known only in alcoholic solution, being decomposed by evaporation. The *hyperacid* salt, with 12 at. As^2S^5, is prepared like the corresponding potassium-salt.

Sulpharsenate of Magnesium.—The *tribasic* salt, Mg^3AsO^4 or $3Mg^2S.As^2S^5$, is obtained by adding sulphydrate of magnesium to a solution of the neutral salt as long as sulphuretted hydrogen continues to escape, and afterwards evaporating the solution, or if it be not too dilute, cooling it quickly down. It forms colourless radiating crystals, which become moist on exposure to the air. Alcohol decomposes them, extracting the neutral salt and leaving a compound of 1 at. As^2S^5 with more than 3 at. Mg^2S, which is nearly insoluble in water. The same compound remains as a white unfused mass, when the neutral salt is heated to redness in a retort. Potash added to the aqueous solution of the tribasic salt precipitates magnesia, and forms a solution of tribasic sulpharsenate of potassium.—The *neutral salt*, $2Mg^2S.As^2S^5$, is a non-crystalline, lemon-yellow mass, which does not absorb water from the air, dissolves in water to any amount, and is precipitated from the solution by alcohol.

Sulpharsenate of Magnesium and Ammonium, $(NH^4)Mg^2AsS^4$ (?)—Precipitated on adding alcohol to an aqueous solution of the mixed sulpharsenates of magnesium and ammonium, in delicate white needles, which, when exposed to the air, give off sulphuretted hydrogen and turn yellow. It dissolves easily in water.

Sulpharsenate of Manganese.—The *neutral salt*, $2Mn^2S.As^2S^5$, is obtained by digesting recently precipitated sulphide of manganese with water, trisulphide of arsenic and sulphur, partly dissolving in the water and partly remaining at the bottom in the form of a lemon-yellow powder, which however dissolves in a larger quantity of water. The solution when evaporated, yields sulphur, and afterwards deposits a lemon-yellow mass, no longer completely soluble in water. The neutral salt is likewise obtained, but mixed with arsenate of manganese, when carbonate of manganese is boiled with water and trisulphide of arsenic and sulphur. Manganous salts are not precipitated by sulpharsenate of sodium. A *sexbasic salt*, $6Mn^2S.As^2S^5$, is produced by digesting the yellow powder of the neutral salt in strong ammonia. It is a brick-red powder, somewhat soluble in water, and, when ignited at one point, continues to burn.

Sulpharsenates of Mercury.—The *mercuric salt*, $2Hg^2S.As^2S^5$, is precipitated from mercuric chloride both by basic and by neutral sulpharsenate of sodium, as a dark yellow substance, which retains its colour after drying. It sublimes undecomposed, and yields a powder of the colour of cinnabar. The *mercurous salt*, $2Hg^4S.As^2S^5$, or $Hhg^4As^2S^7$, is precipitated black from solutions free from mercuric oxide; if the latter is present, the precipitate is brownish-yellow, and becomes darker in drying. When distilled, it decrepitates violently and gives off mercury, and at a higher temperature yields a sublimate of the mercuric salt just described.

Molybdic Acid is is not precipitated by sulpharsenate of sodium.

Sulpharsenate of Nickel.—Nickel-salts, if not too dilute, immediately yield a black precipitate, with neutral or basic sulpharsenate of sodium. Very dilute solutions first assume a yellow-brown colour, then yield a precipitate.

Sulpharsenate of Platinum.—The neutral and basic sodium-salts do not precipitate platinum-solutions, but merely colour them dark-brown. Ferrous sulphate added to the brown liquid, throws down a black-brown substance, while the solution becomes colourless.

Sulpharsenate of Potassium.—The *tribasic salt*, $3K^2S.As^2S^5$, or K^3AsS^4, is deposited as an oily concentrated solution, on mixing the aqueous solution of the neutral salt with alcohol. When dried at a gentle heat, it leaves a fibrous deliquescent mass.

The *neutral* or *dibasic* salt, $2K^2S.As^2S^5$, or $K^4As^2S^7$, is produced by saturating an aqueous solution of dipotassic arsenate with hydrosulphuric acid and evaporating in vacuo. The residue is a viscid, yellowish, somewhat crystalline mass, which does not dry up completely, but on exposure to the air first liquefies and then solidifies in a crystalline mass of rhombic tablets.

The *monobasic* or *acid* salt, $K^2S.As^2S^5$, or $KAsS^3$, remains dissolved when the aqueous solution of the neutral salt is precipitated with alcohol. The solution is decomposed by evaporation, and deposits crystals of persulphide of arsenic (see p. 386).—2 Aqueous sulphide of potassium dissolves at ordinary temperatures, more than ½ at. but less than 1 at. of pentasulphide of arsenic. The solution, when evaporated in the air, first becomes covered with a film of sulphur, then deposits a red crust, and by this loss of sulphide of arsenic, is converted into the dibasic salt, which dries up first to a stiff syrup and then to a lemon-yellow mass.

A *hyper-acid* salt, $K^2S.12As^2S^5$, is precipitated when the solution of the neutral salt is decomposed by carbonic acid; similarly on passing hydrosulphuric acid gas through monopotassic arsenate.—It is a yellow powder, containing 2·9 sulphide of potassium and 97·1 pentasulphide of arsenic. (Berzelius.)

Sulphoxarsenate of Potassium. $(K^2O.2H^2O)As^2S^3O^2 = (K^2H^4)As^2S^3O^4$. — Produced when sulphuretted hydrogen is rapidly passed through a cold saturated solution of dipotassic arsenate (p. 383). The liquid first turns yellow, then deposits a small quantity of trisulphide of arsenic mixed with sulphur, and ultimately a colourless crystalline salt. When a certain quantity of this salt has been formed, caustic potash is to be added to the liquid, and the stream of sulphuretted hydrogen continued: by this means, an additional quantity is obtained. The greater part of the sulphide of arsenic must then be rinsed away with the mother-liquor, and the salt washed with very small quantities of water, pressed, and dried in vacuo. It crystallises in small white elongated prisms, sometimes 1 or 2 centimetres long, slightly soluble in water. The dry salt is permanent in the air, and gives up all its water at 170° C., without melting. It fuses over the spirit-lamp, giving off, first arsenic sulphide and then metallic arsenic. The aqueous solution decomposes rapidly at a boiling heat, giving off hydrosulphuric acid and depositing sulphur. If hydrochloric acid be then added, a precipitate of sulphide of arsenic is obtained. From the salt itself, hydrochloric acid precipitates nothing but sulphur, and the precipitation is complete; the filtrate then contains arsenious acid. Lead-salts added to the solution give a white precipitate, which soon turns black. The acid of this salt, $H^6As^2S^3O^4$ (arsenic acid, having part of its oxygen replaced by sulphur), cannot be obtained in the free state. If the lead-salt, immediately after its formation, be collected on a filter and mixed with a quantity of dilute sulphuric acid less than sufficient to decompose it completely, a strongly acid liquid is obtained, which gives no precipitate with barium-salts; but it quickly decomposes and deposits sulphide of arsenic. (Bouquet and Cloez, Ann. Ch. Phys. [3] xiii. 44.)

Sulpharsenate of Silver.—Both the *neutral* and *basic* salts are precipitated from silver-solutions, with brown colour, turning black in drying; the precipitates are very slow in settling down. When they are heated in the air, the sulphide of arsenic burns away, and sulphide of silver remains; but if heated to redness in close vessels, they fuse without giving off sulphur or sulphide of arsenic, and on cooling solidify in the form of a grey, somewhat ductile cake, exhibiting metallic lustre.

Sulpharsenate of Sodium. a. Tribasic salt. $3Na^2S.AsS^5 + 15H^2O = 2Na^3AsS^4 + 15H^2O$.—Obtained: 1. By precipitating a solution of the dibasic salt with alcohol.—2. By leaving a mixture of the dibasic salt *b* and sulphydrate of sodium to evaporate.—3. By digesting the alcoholic solution of pentasulphide of sodium with orpiment, pouring the liquid off, washing the residue with alcohol, then dissolving out the tribasic salt with water, and leaving the solution to crystallise.—4. By dissolving pentasulphide of arsenic in aqueous soda-solution, and leaving the liquid to crystallise. The crystals obtained by either of these methods are washed on a filter with alcohol, then pressed and dried (Berzelius).—*5.* By boiling 1 pt. of sulphur, 1½ pt. of orpiment, and 8 pts. of crystallised carbonate of soda with water, and purifying the crystals obtained from the filtrate by recrystallisation (Rammelsberg, Pogg. Ann. liv. 238). By method (1) the salt is obtained in snow-white crystals; by (4) in ill-defined rhomboïdal tables. It crystallises by slow cooling from a hot aqueous solution, in irregular six-sided prisms, with two of their lateral edges more acute than the rest; by spontaneous evaporation or very slow cooling, in transparent rhombic prisms with dihedral summits resting on the acute lateral edges; and by still slower cooling, till the temperature falls below 0° C., in white, opaque, rhombic octahedrons. The opaque crystals are milk-white; the transparent crystals are yellowish, and have somewhat of a diamond lustre. (Berzelius.)

The salt when dry is permanent in the air; even in vacuo over oil of vitriol, it does not give up its water till gently heated; it then becomes milk-white; when more strongly heated, it gives off a small quantity of hydrosulphuric acid, and turns yellow. Heated in a retort, in fuses it its water of crystallisation, forming a very pale yellow liquid, then gives off water, and is converted into a white salt, which, when more strongly heated, decrepitates slightly, evolves the remaining water and a small quantity of hydrosulphuric acid, and fuses to a dark red liquid; on cooling, this liquid solidifies and forms the yellow anhydrous compound, Na^3AsS^4 (Berzelius). It is decomposed completely by boiling with sulphate of copper, yielding a precipitate of sulphide of copper, while soda, sulphuric acid, and arsenic acid remain in solution:

$$Na^3AsS^4 + 4Cu^2SO^4 + 4H^2O = 4Cu^2S + Na^3AsO^4 + 4H^2SO^4.$$

A similar decomposition takes place with acetate of lead; but the precipitated sulphide of lead [if the acetate is in excess], is mixed with arsenate of lead, because that salt is insoluble in acetic acid (Rammelsberg). The salt dissolves easily and abundantly in water. (Berzelius.)

b. Dibasic or *Neutral salt.* $2Na^2S.As^2S^5 = Na^4As^2S^7$.—The aqueous solution of disodic arsenate saturated with hydrosulphuric acid gas, and then left to evaporate spontaneously, yields a viscid liquid, and afterwards, if gently heated, a dry lemon-yellow mass. This substance melts at a moderate heat, forming a very pale yellow liquid (losing water at the same time if warmed in an open vessel), and on cooling solidifies in a yellow mass, which softens when exposed to the air. (Berzelius.)

c. Monobasic salt. $Na^2S.As^2S^5 = NaAsS^3$.—When the tribasic salt is prepared with alcohol according to method (1), the supernatant alcoholic solution contains the mono-basic salt. On distilling off the alcohol, the liquid often deposits persulphide of arsenic in beautiful crystals.

d. Hyper-acid salt, $Na^2S.12As^2S^5$.—Yellow powder, obtained like the potassium compound. (Berzelius.)

Sulpharsenate of Sodium and Ammonium, $(NH^4)^3AsS^4.Na^3AsS^4$, is obtained by mixing the solutions of the two basic salts with alcohol, and cooling slowly, whereupon it collects on the sides of the vessel in small four-sided tables; or more easily by dissolving sal-ammoniac in an exactly proportional quantity of the basic sodium-salt and leaving the solution to evaporate; it then separates in yellowish six-sided prisms, permanent in the air, and much more soluble in water than the sodium-salt. When distilled, it gives off sulphide of ammonium with a little water, leaving sulpharsenite of sodium.

The neutral sulpharsenates of sodium and ammonium dry up to a yellow mass when mixed.

Sulpharsenate of Sodium and Potassium.—Very regular four-sided tables, having a faint yellowish colour.

Sulpharsenate of Strontium.—The *neutral* salt is obtained in the same manner as the barium-compound. On mixing the solution with alcohol, the *basic* salt is precipitated, sometimes as a syrup, sometimes as a white powder, according as it is more or less purified from the neutral salt.

Sulpharsenates of Tin.—Both the neutral and basic sodium-salts form with *stannous* chloride, a dark chestnut-brown precipitate; with *stannic* chloride, pale yellow gummy precipitates, becoming orange-yellow when dry.

Uranic Sulpharsenate.—The *neutral* salt, $2U^4S^3.As^2S^5$ or $(U^2S)^4As^2S^7$, is a dingy yellow precipitate; the basic salt has a somewhat darker colour. Both dissolve with dark brown colour in excess of the precipitant.

Vanadic salts give no precipitate with sulpharsenate of sodium; but the blue solution is decolorised.

Sulpharsenate of Yttrium.—Resembles the glucinum-salt.

Sulpharsenate of Zinc.—The *neutral* salt is a light yellow precipitate, the *basic* salt till lighter; both are orange-yellow when dry.

Sulpharsenate of Zirconium.—Solutions of zirconium-salts are precipitated, though not immediately, both by basic and by neutral sulpharsenate of sodium; the precipitate is lemon-yellow while moist, orange-yellow after drying. Acids do not extract zirconia from it.

ARSENICAL COBALT, COPPER, IRON, &c. See the several metals.

ARSENICAL PYRITES. See IRON, ARSENIDES OF.

ARSENICAL PYROPHORUS. Arsenite of barium ignited with gum-tragacanth, is said by Osann to yield a greyish-yellow pyrophoric mixture.

ARSENIC-RADICLES (ORGANIC). Arsenic unites with the alcohol-radicles, forming compounds analogous to those of antimony, and containing 1 at. arsenic, combined with 1, 2, 3, or 4 at. of the organic radicle. The following is a list of the compounds of this class at present known. Those to which no formulæ are assigned, have been but imperfectly studied.

Arsenides of Allyl.

Arsenides of Amyl.

Arsenides of Ethyl:

Arsenethyl	$As(C^2H^5)$
Arsendiethyl, or Ethyl-cacodyl	$As(C^2H^5)^2$
Arsentriethyl, or Triethylarsine	$As(C^2H^5)^3$
Arsenethylium, or Tetrethylarsonium . . .	$As(C^2H^5)^4$

Arsen-bromethyl-triethylium	$As(C^2H^4Br)(C^2H^5)^3$
Arsenvinyl-triethylium	$As(C^2H^3)(C^2H^5)^3$
Ethylene-hexethyl-diarsonium	$As^2(C^2H^4)''(C^2H^5)^6$
Ethylene-triethylarsammonium	$AsNH^3(C^2H^4)''(C^2H^5)^3$
Aurarsenethylium	$As(C^2H^5)^3Au$
Platarsenethylium	$As(C^2H^5)^3Pt$

Arsenides of Methyl:

Arsenmethyl	$As(CH^3)$
Arsendimethyl, or Cacodyl	$As(CH^3)^2$
Arsentrimethyl, or Trimethylarsine . . .	$As(CH^3)^3$
Arsenmethylium, or Tetramethylarsonium . .	$As(CH^3)^4$
Arsentrimethyl-ethylium	$As(CH^3)^3(C^2H^5)$
Arsendimethyl-diethylium	$As(CH^3)^2(C^2H^5)^2$
Arsenmethyl-triethylium	$As(CH^3)(C^2H^5)^3$
Arsendimethyl-diamylium	$As(CH^3)^2(C^5H^{11})^2$

Arsenide of Tetryl (or Butyl).

Arsenide of Trityl (or Propyl).

These compounds are produced, like the antimonides of the alcohol-radicles, by distilling the iodides of these radicles with arsenide of potassium or sodium. Arsendimethyl, or cacodyl, is likewise formed by distilling a mixture of arsenious oxide and an alkaline acetate, and was obtained in this manner by Cadet, so long ago as 1760. The di-trityl and di-tetryl compounds appear to be produced in a similar manner, by distilling arsenious oxide with an alkaline valerate or butyrate. The compounds containing 2 and 3 at. of alcohol-radicle, *e. g.* cacodyl and arsentriethyl, have been obtained in the free state; the rest only in combination.

The compounds containing 1 at. alcohol-radicle, such as $As(CH^3)$, are di-atomic and tetr-atomic, uniting with 2 and 4 at. Cl, I, &c.; those with 2 at. alcohol-radicle, cacodyl, for example, are mono- and tri-atomic; those with 3 at. alcohol-radicle, $As(C^2H^5)^3$, for example, are di-atomic; and those which contain 4 at. alcohol-radicle, *e. g.* $As(C^2H^5)^4$, are monatomic and triatomic. (See ORGANO-METALLIC BODIES.)

Arsenides of Allyl. When iodide of allyl is heated with arsenide of potassium, a number of liquid products are formed, having an extremely offensive odour, and rising gradually in boiling point, so that their separation cannot well be effected, and at the same time, a solid crystalline mass is formed, which appears to be the iodide of arsenallylium or tetrallylarsonium, $As(C^3H^5)^4I$. (Cahours and Hofmann, Phil. Trans. 1857, p. 335.)

Arsenides of Amyl. Iodide of amyl distilled with arsenide of potassium, yields compounds analogous to the arsenides of ethyl and methyl. (Cahours and Riche.)

Arsenides of Ethyl.*

Three of these compounds, viz. *arsendiethyl*, $As(C^2H^5)$, *arsentriethyl*, $As(C^2H^5)^3$, and *arsenethylium*, $As(C^2H^5)^4$, are obtained by a process similar to that already described for the preparation of stibtriethyl (p. 341), viz. by subjecting arsenide of sodium mixed with quartz-sand, to the action of iodide of ethyl in an atmosphere of dry carbonic acid gas. The action takes place without external heating, and when it is finished, the resulting arsenides of ethyl may be separated one from the other either by fractional distillation, or by treatment with ether. *Arsenethyl*, AsC^2H^5, is obtained by the decomposition of arsendiethyl.

ARSENETHYL, or ARSENMONETHYL, $As(C^2H^5) = AsE$.—This radicle is not known in the free state; but the di-iodide is obtained (together with iodide of ethyl), by the action of 2 at. iodine on 1 at. iodide of arsendiethyl, or of 3 at. iodine on 1 at. arsendiethyl:

$$AsE^2I + I^2 = EI + AsEI^2$$
$$AsE^2 + I^3 = EI + AsEI^2.$$

The di-iodide distilled with 2 at. *iodine*, yields tri-iodide of arsenic ($AsEI^2 + I^2 = EI + AsI^3$). Treated with excess of *oxide of silver* and *water*, it is converted into arsenmonethylic acid, $As(C^2H^5)H^2O^3$. (Cahours, Compt. rend. l. 1022; Rép. Chim. pure, ii. 256.)

ARSENDIETHYL, or ETHYL-CACODYL, $As(C^2H^5)^2$, is best obtained by treating arsenide of sodium with excess of iodide of ethyl, in the manner just mentioned,

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* Landolt, Ann. Ch. Pharm. lxxxix. 301; xcii. 365; Gm. ix. 70; Gerh. ii. 949.—Cahours and Riche, Compt. rend. xxxvi. 1001; xxxix. 541; Jahresber. f. Chem. 1853, 487; 1854, 530.—Cahours, Compt. rend. xlix. 87; Jahresber. 1859, 430; further, Compt. rend. l. 1022; Rép. Chim. pure, ii. 255.

digesting the crude distillate with ether, mixing the ethereal extract with absolute alcohol, expelling the ether by evaporation, and mixing the alcoholic solution with water, which precipitates arsendiethyl, and retains in solution the iodide of arsenethylium, formed by the union of arsentriethyl with the excess of iodide of ethyl.

Arsendiethyl is an oily liquid, having a faint yellowish colour, strong refracting power, and a very disagreeable, pungent, alliaceous odour. It sinks in water without mixing. Boils between 185° and 190° C. It absorbs oxygen rapidly from the air giving off vapours of arsenious oxide, and if it has been separated by fractional distillation, it takes fire when a drop of it is let fall on wood or paper; but if it has been precipitated by water from the alcoholic solution, it does not take fire till heated to 180° C. It is rapidly oxidised by strong nitric acid, with evolution of light and heat, less completely by dilute nitric acid, which also forms with it a red substance analogous to Bunsen's *erythrarsin*. Arsendiethyl reduces the noble metals, silver, mercury, &c. from their solutions, and is at the same time converted into *arsendiethylic acid*, $As(C^2H^5)^2HO^2$.

Arsendiethyl also unites directly with *chlorine*, *bromine*, *iodine*, and *sulphur*. These compounds are liquids having a peculiarly repulsive and persistent odour, and attacking the eyes strongly; continued exposure to it produces headache and other unpleasant symptoms. The iodide, $As(C^2H^5)^2I$, is prepared by saturating an ethereal solution of arsendiethyl with an ethereal solution of iodine, and evaporating the ether. It is a yellow oil, insoluble in water, but soluble in alcohol and ether. The alcoholic solution mixed with nitrate or sulphate of silver, yields a precipitate of iodide of silver, and a solution of nitrate or sulphate of arsendiethyl.

On gradually adding a dilute alcoholic solution of *mercuric chloride* to an alcoholic solution of arsendiethyl, a white precipitate is formed, which however disappears on boiling, and the solution yields on cooling a crystalline powder, consisting of $2Hg^2O.As(C^2H^5)^2Cl^2$. This salt is inodorous, sparingly soluble in cold water and in alcohol, more soluble in boiling water: it is decomposed by strong nitric acid. Two other crystalline compounds are formed at the same time, in small quantity.

Arsendiethylic Acid. $As(C^2H^5)^2HO^2$.—When arsendiethyl is triturated with red oxide of mercury under water, mercury separates out, and a solution of arsendiethylate of mercury is formed; and by precipitating the mercuric oxide with baryta-water, removing the excess of baryta by carbonic acid, decomposing the filtered solution of arsendiethylate of barium with sulphuric acid, and evaporating, arsendiethylic acid is obtained in crystals. This acid is also produced by the direct oxidation of arsendiethyl, as when that substance is left for some time in a loosely stoppered bottle; also, when its alcoholic solution is exposed to the air, or more quickly when that solution is shaken up with oxygen gas. The crystals contain $As(C^2H^5)^2HO^2$. They are inodorous, have a slightly acid, afterwards bitter taste, deliquesce in the air, and dissolve readily in water and alcohol, sparingly in ether. They melt at 190° C., forming an oily liquid, which solidifies in a crystalline mass on cooling; but at higher temperatures, they are decomposed, with evolution of arsenious oxide and stinking arsenical products. The acid is not attacked by nitric acid, aqua-regia, or by the milder reducing agents, such as sulphurous acid, and ferrous sulphate; but phosphorous acid reduces it, forming a pungent oily liquid, probably the oxide of arsendiethyl. The aqueous solution of the acid readily decomposes carbonates, and precipitates *ferric*, *mercurous*, and *cupric* salts; also acetate of *lead*. The *mercuric* salt is a deliquescent crystalline mass. The *barium*-salt, obtained by saturating the aqueous acid with baryta-water and evaporating, contains $2BaHO.3As(C^2H^5)^2HO^2 + \frac{1}{2}H^2O$; the water of crystallisation is not completely given off at 120° C.

ARSENTRIETHYL, or **TRIETHYLARSINE**. $As(C^2H^5)^3$.—This is the chief product of the action of iodide of ethyl on arsenide of sodium, and is easily separated from the other products by fractional distillation in an atmosphere of carbonic anhydride: it passes over between 140° and 180° C. It is also produced by the action of trichloride of arsenic on zinc-ethyl (Hofmann and Cahours, Compt. rend. xli. 831). It is a colourless, mobile, strongly refracting liquid, having a disagreeable odour, like that of arsenetted hydrogen. Specific gravity 1·151 at 16·7° C. Under a pressure of 736 mm. it begins to boil at 140° C., but the boiling point quickly rises to 180°, a small quantity of arsenic separating at the same time. Its vapour-density is, by experiment, 5·2783; by calculation (2 vol.) 5·6156.

Arsentriethyl fumes and becomes heated in contact with the air, but seldom takes fire unless it is heated; the products of the oxidation are arsenious anhydride, carbonic anhydride and water. The oxidation takes place slowly, even under water in a closed vessel. Strong *nitric acid* oxidises it rapidly, with vivid combustion and explosion, but nitric acid of specific gravity 1·42, dissolves it slowly, giving off nitric oxide, and producing nitrate of arsentriethyl; but no red compound is formed. This character serves to distinguish arsentriethyl from arsendiethyl: a further distinction is afforded by the fact that arsentriethyl does not reduce the noble metals from their solutions.

Arsentriethyl is a diacid radicle, 1 at. of it uniting with 2 at. of a monatomic acid radicle, *e. g.* $As(C^2H^5)^3.I^2$, and with one at. of a diatomic acid radicle, *e. g.* $As(C^2H^5)^3.S$.

Bromide of Arsentriethyl, $As(C^2H^5)^3Br^2$, is obtained by mixing the alcoholic solutions of bromine and arsentriethyl, the former in slight excess, and evaporating at 100° C. It is a yellowish, deliquescent, crystalline mass, the odour of which excites sneezing. When heated it melts, and burns with a white flame. It is decomposed by chlorine, by nitric acid, and by strong sulphuric acid.

Iodide of Arsentriethyl, $As(C^2H^5)^3I^2$, is obtained by mixing the ethereal solutions of its constituents: it is then deposited in yellow flakes which rapidly turn brown and liquefy on exposure to the air. It dissolves readily in water and alcohol, sparingly in ether.

The *chloride* appears to be formed in small quantity by the action of hydrochloric acid on the oxide or sulphide.

Oxide of Arsentriethyl, $As(C^2H^5)^3O$, is produced when an ethereal solution of arsentriethyl is left to evaporate in the air; but it may be obtained in a state of greater purity by exhausting the mass produced by the action of iodide of ethyl on arsenide of sodium, first with ether, and then with alcohol, evaporating the alcoholic solution, and distilling the residue. It is an oily liquid, heavier than water and not miscible with it, but soluble in alcohol, and precipitated from the alcoholic solution by water. It dissolves in dilute nitric acid, but not in sulphuric or hydrochloric acid. When left for some weeks in a loosely stoppered bottle, it is gradually converted into an inodorous crystalline substance [probably arsentriethylic acid].

Sulphide of Arsentriethyl, $As(C^2H^5)^3S$, is obtained by boiling an ethereal solution of arsentriethyl with flowers of sulphur. It forms beautiful prismatic crystals, which may be purified by recrystallisation from boiling water or alcohol, or better by solution in warm ether, and gradual evaporation. It has a bitter taste, but is quite inodorous when pure. It melts at 100° C., and decomposes at a higher temperature, giving off spontaneously inflammable vapours. It is rapidly oxidised by strong *nitric acid*. Dilute *hydrochloric acid* decomposes it partially, giving off small quantities of hydrosulphuric acid and *chloride of arsentriethyl*, recognisable by its peculiarly pungent odour. It is not decomposed by boiling with *caustic potash*. Its aqueous solution precipitates *metallic solutions* like an alkaline sulphide.

ARSENETHYLIUM or **TETRETHYLARSONIUM**, $As(C^2H^5)^4$, is not known in the free state, but is obtained as an iodide by the action of iodide of ethyl on arsentriethyl; also, according to Cahours and Riche, by the action of metallic arsenic on iodide of ethyl. Its compounds are analogous to those of tetrethylium, and contain 1 at. arsenethylium with 1 at. of a monobasic acid radicle, or 2 at. arsenethylium with 1 at. of a dibasic acid radicle. The *hydrate*, obtained by the action of oxide of silver on the iodide, is a fixed base resembling hydrate of potassium, and dissolves readily in acids, forming salts which crystallise readily, are permanent in the air, have a bitter taste, and do not appear to be poisonous. In this respect, they differ remarkably from the compounds of arsendiethyl and arsentriethyl.

Bromide of Arsenethylium, $As(C^2H^5)^4Br$, is a white, deliquescent, saline mass, which dissolves easily in water and alcohol, and exhibits with acids and metallic salts, the same reactions as bromide of potassium.

Chloride of Arsenethylium forms crystals containing $As(C^2H^5)^4Cl.4H^2O$, which dissolve readily in water and alcohol, but are insoluble in ether. The aqueous solution immediately precipitates chloride of silver from the nitrate and forms an insoluble double salt with *mercuric chloride*. With *dichloride of platinum* it forms the compound $As(C^2H^5)^4Cl.PtCl^2$, which dissolves very sparingly in cold, somewhat more readily in boiling water.

Iodide of Arsenethylium, $As(C^2H^5)^4I$, forms large colourless crystals, easily soluble in water and alcohol, but insoluble in ether. When heated, they fall to powder, give off spontaneously inflammable vapours, and yield a sublimate of arsenic. They are decomposed by nitric and by sulphuric acid. A compound of *iodide of arsenethylium* and *iodide of arsenic* is obtained by heating iodide of ethyl to 100° C. with metallic arsenic:

$$4C^2H^5I + As^2 = As(C^2H^5)^4I.AsI^3.$$

This compound forms splendid red tables, which are decomposed by distillation, yielding iodide of arsentriethyl and iodide of arsendiethyl (Cahours and Riche, Compt. rend. xxxix. 546). It is also decomposed by hot potash-solution, yielding iodide of arsenethylium, iodide of potassium, and arsenite of potassium. Iodide of arsenethylium heated with *iodide of zinc*, yields the compound $As(C^2H^5)^4I.ZnI$; similarly with *iodide of cadmium*.

Arsenethylium likewise forms a *tri-iodide*, $As(C^2H^5)^4I^3$, analogous to the tri-iodide of tetrethylium discovered by Weltzien. (Cahours, Compt. rend. l. 1022; Rép. Chim. pure, ii. 255.)

The *sulphate*, $[As(C^2H^5)^4H]SO^4$, is formed by precipitating a solution of the iodide with an acid solution of sulphate of silver. Granular crystals, easily soluble in water and alcohol, sparingly in ether, and decomposed by heat, with evolution of acid vapours.

ARSEN-BROMETHYL-TRIETHYLIUM, or BROMETHYL-TRIETHYLARSONIUM. $As(C^2H^4Br)(C^2H^5)^3$.—The *bromide* of this radicle is obtained by heating a mixture of triethylarsine with a very large excess of dibromide of ethylene, in sealed tubes at a temperature not above 50° C., extracting the product with water, evaporating and recrystallising from boiling alcohol. It forms beautiful crystals, extremely soluble in water, the form of which exactly resembles that of the corresponding phosphonium-compound (see PHOSPHORUS-RADICLES, ORGANIC). It contains the elements of 1 at. dibromide of ethylene and 1 at. triethylarsine:

$$C^2H^4Br^2 + As(C^2H^5)^3 = [As(C^2H^4Br)(C^2H^5)^3]Br.$$

Nitrate of silver added in excess to the solution of the bromide, precipitates only half the bromine; the other half is precipitated on treating the filtrate with ammonia (see AMMONIUM-BASES, p. 196). The platinum-salt of this radicle forms splendid yellow needles, sparingly soluble even in boiling water. (A. W. Hofmann, Proc. Roy. Soc. xi. 62.)

ARSENVINYL-TRIETHYLIUM, or VINYL-TRIETHYLARSONIUM. $As(C^2H^3)(C^2H^5)^3$.—The hydrated oxide of this radicle is obtained by treating bromide of bromethyl-triethylarsonium with excess of oxide of silver:

$$[As(C^2H^4Br)(C^2H^5)^3]Br + Ag^2O = \left.\begin{matrix}As(C^2H^3)(C^2H^5)^3\\H\end{matrix}\right\}O + 2AgBr.$$

A strongly alkaline solution is obtained which, when treated with hydrochloric acid and precipitated by dichloride of platinum, yields beautiful, rather soluble octahedrons, containing $[As(C^2H^3)(C^2H^5)^3]Cl.PtCl^2$. (Hofmann, *loc. cit.*)

ETHYLENE-HEXETHYLDIARSONIUM. $As^2(C^2H^4)''(C^4H^5)^6$.—Obtained as a dibromide or dichloride, by digesting the bromide or chloride of bromethyl-triethylarsonium with triethylarsine at 150° C. for two hours. The dibromide $[As^2(C^2H^4)''(C^2H^5)^6]''Br^2$, treated with oxide of silver, yields the hydrate $\left.\begin{matrix}[As^2(C^2H^4)''(C^2H^5)^6]''\\H^2\end{matrix}\right\}O^2$, which is a powerful alkali, and forms with acids a series of beautiful salts:

The *platinum-salt*. $[As(C^2H^4)''(C^2H^5)^6]''Cl^2.2PtCl^2$, is a pale yellow crystalline precipitate, soluble in water and in boiling hydrochloric acid, from which it crystallises on cooling.

The *gold-salt*, $[As^2(C^2H^4)''(C^2H^5)^6Cl^2.2AuCl^3$, crystallises from hydrochloric acid in gold-coloured plates. (Hofmann, *loc. cit.*)

ETHYLENE-TRIETHYLARSAMMONIUM $\left[(C^2H^4)''\begin{matrix}(C^2H^5)^3As\\H^3N\end{matrix}\right]''$. The *dibromide* of this radicle is obtained by heating the bromide of bromethyl-triethylarsonium with ammonia to 100° C. for two hours. Treated with oxide of silver, it yields the caustic base $\left.\begin{matrix}[(C^2H^4)''(C^2H^5)^3H^3AsN]''\\H^2\end{matrix}\right\}O^2$. The *platinum-salt* $\left[(C^2H^4)''\begin{matrix}(C^2H^5)^3As\\H^3N\end{matrix}\right]''Cl^2.2PtCl^2$, crystallises from hydrochloric acid in needles, sparingly soluble in boiling water. The *gold-salt* crystallises from hydrochloric acid in golden-yellow plates. (Hofmann, *loc. cit.*)

The reactions by which the last four bases are obtained are precisely similar to those which yield the corresponding compounds of the phosphorus series, and will be more fully considered in the article PHOSPHORUS-RADICLES (ORGANIC), in which also the *phospharsoniums*, containing both phosphorus and arsenic, will be described.

AURARSENETHYLIUM, $As(C^2H^5)^3Au$, and PLATARSENETHYLIUM, $As(C^2H^5)^3Pt$.—The chlorides of these compounds are obtained in fine crystals by treating an alcoholic solution of arsentriethyl with trichloride of gold and dichloride of platinum respectively. (Hofmann, Ann. Ch. Pharm. cvii. 357.)

Arsenides of Methyl.

Cadet discovered, in 1760, that by distilling acetate of potassium with arsenious oxide, a fetid brown-red liquid is obtained, which takes fire on exposure to the air. But the nature of this liquid was not understood till Bunsen undertook its examination, and showed that it contained a metalloïdal radicle, AsC^2H^6, to which he gave the the name Cacodyl (from κακος, bad) on account of its extremely poisonous qualities.

Bunsen, moreover, isolated this radicle, and prepared a great number of its compounds, showing that, in its chemical relations, it is precisely analogous to a simple metal. This was the second instance of the isolation of a compound radicle, the separation of cyanogen by Gay-Lussac having been the first. It has since been shown by Cahours and Riche (Compt. rend. xxxix. 341), that cacodyl or arsendimethyl, $As(CH^3)^2$ may be obtained by the action of iodide of methyl on arsenide of sodium, other arsenides of methyl, viz. $As(CH^3)^3$ and $As(CH^3)^4$ being formed at the same time. Lastly, Baeyer, has obtained several compounds of arsenmonomethyl, $AsCH^3$.

ARSENMETHYL, or ARSENMONOMETHYL, $AsCH^3 = AsMe$.—(Baeyer, Ann. Ch. Pharm. cvii. 279.) The *dichloride* of this radicle (which is not known in the separate state) is produced either by the decomposition of trichloride of arsendimethyl (cacodyl) by heat:

$$\underset{\text{Trichloride of cacodyl.}}{AsMe^2Cl^3} = \underset{\text{Dichloride arsenmethyl.}}{AsMeCl^2} + \underset{\text{Chloride of methyl.}}{MeCl}$$

or by the action of hydrochloric acid on cacodylic acid:

$$AsMe^2O^2H + 3HCl = AsMeCl^2 + MeCl + 2H^2O.$$

When a stream of dry hydrochloric acid gas is passed over cacodylic acid, basic perchloride of cacodyl (p. 408) is first formed; but by the continued action of the gas, this compound is also decomposed, with separation of water, which passes over in the distillate, together with the dichloride.

Dichloride of arsenmethyl is a colourless, heavy, mobile liquid, having a strong refracting power. It boils at 133° C., which is nearly the boiling point of trichloride of arsenic. It does not fume in the air, and is not decomposed by water, but dissolves rather freely in that liquid. It forms a white precipitate with sulphuretted hydrogen. The vapour of this compound exerts a most violent action on the mucous membranes: on smelling it, the eyes, nose, and the whole face swell up, and a peculiar lancinating pain is felt, extending down to the throat.

Tetrachloride of Arsenmethyl, $AsMeCl^4$.—When chlorine is passed over a mixture of dichloride of arsenmethyl and sulphide of carbon cooled to − 10° C., large crystals are obtained, which immediately decompose at temperatures near the freezing point of water, yielding chloride of methyl and trichloride of arsenic: hence the crystals consist of tetrachloride of arsenmethyl:

$$AsCH^3Cl^4 = AsCl^3 + CH^3Cl.$$

Chlorobromide of Arsenmethyl, $AsMeClBr$, appears to be produced by the spontaneous decomposition of chlorodibromide of cacodyl, bromide of methyl being given off at the same time:

$$AsMe^2ClBr^2 = AsMeClBr + MeBr;$$

but the liquid product of the decomposition is too unstable to admit of an examination of its properties.

Iodide of Arsenmethyl, $AsCH^3I^2$, is obtained by the action of hydriodic acid on the alcoholic solution of the oxide (see below). The liquid yields by spontaneous evaporation, shining yellow needles of the iodide an inch long. They are not altered by contact with the air, but appear to decompose slowly by keeping (Baeyer). The same compound is produced by the action of 2 at. iodine on iodide of cacodyl, or of 3 at. iodine on free cacodyl, iodide of methyl being set free at the same time. (Cahours, Compt. rend. l. 1022):

$$AsMe^2I + I^2 = MeI + AsMeI^2$$
$$AsMe^2 + I^3 = MeI + AsMeI^2$$

It melts at 25° C., and often remains liquid for a long time after cooling. It is colourless and volatile without decomposition above 200° C. It is but slightly soluble in water, but dissolves readily in alcohol, ether, and sulphide of carbon; less readily, however, in presence of free hydriodic acid. Hydrochloric acid converts it into chloride, and hydrosulphuric acid into sulphide of arsenmethyl. (Baeyer.) Distilled with 2 at. iodine, it yields iodide of methyl, and triiodide of arsenic, AsI^3. (Cahours.)

Oxide of Arsenmethyl, $As(CH^3)O$, is produced by the action of potash on the dichloride:

$$AsMeCl^2 + 2KHO = AsMeO + 2KCl + H^2O;$$

but on distilling the product with excess of potash, complete decomposition takes place and oxide of cacodyl is obtained, instead of oxide of arsenmethyl (see below).

A better result is obtained by saturating the dichloride with carbonate of potassium, then adding an excess of the latter, extracting with absolute alcohol, distilling off the alcohol in a stream of carbonic acid, digesting the residue in sulphide of carbon, which leaves chloride of potassium and other impurities undissolved, and leaving the clear solution to evaporate. Oxide of arsenmethyl is then obtained in large cubical crystals (not regular, however), which soon become dull, and assume the aspect of white porcelain; sometimes, however, crystals are obtained which retain their transparency, but they are then very imperfectly developed. The oxide is very heavy, permanent in the air, and has a strong odour like that of asafœtida. It dissolves slowly but abundantly in cold water, readily in hot water, also in alcohol, ether, and sulphide of carbon. It melts at 95° C., and remains liquid for a considerable time after cooling. It is decomposed by distillation, and the evolved vapours explode when mixed with air. A portion volatilises, however, with the vapour of water or alcohol. By distillation with hydrate of potassium, it is resolved into arsenious oxide and oxide of cacodyl:

$$4As(CH^3)O = As^2O^3 + As^2(CH^3)^4O.$$

The oxide appears to possess rather basic than acid properties, as it does not unite with baryta, but dissolves readily in acids; its aqueous solution is neutral to vegetable colours. *Hydrochloric acid* added to the concentrated aqueous solution throws down the chloride of arsenmethyl in oily drops; *hydrobromic acid* acts in like manner; *hydriodic acid* produces a yellow precipitate of the iodide; and *hydrosulphuric acid* a white precipitate of the sulphide. The oxide is not acted upon by hydrocyanic acid, but is easily raised to a higher stage of oxidation by *nitric acid*, *mercuric oxide*, or *silver-oxide*. *Chlorine*, *bromine*, and *iodine* added to its solution in sulphide of carbon, form precipitates which soon decompose. Corrosive sublimate does not appear to unite with it.

Arsenmethylic acid. $As(CH^3)H^2O^3$.—The barium-salt of this acid is obtained by decomposing the dichloride of arsenmethyl with a slight excess of silver-oxide; filtering from chloride of silver; treating the filtrate with excess of baryta-water; removing that excess by carbonic acid; evaporating the filtered liquid to dryness over the water-bath; dissolving the residue in a small quantity of water; and precipitating by alcohol. The same salt may be obtained by decomposing the aqueous solution of oxide of arsenmethyl with mercuric oxide (for which purpose the alcoholic distillate obtained in the preparation of the oxide, *vid. sup.* may be used), decomposing the resulting mercurous salt with baryta, and proceeding as before.

By carefully decomposing the barium-salt with sulphuric acid and evaporating the filtrate over the water-bath, arsenmethylic acid is obtained in the form of a laminated mass, resembling precipitated nitrate of urea. It is purified by solution in hot alcohol, and crystallises, on cooling, in large spear-shaped laminæ, composed of small needles, united in arborescent groups, permanent in the air, and not containing any water of crystallisation. It is a strong acid, having a pure, sour, agreeable, taste, and capable of decomposing carbonates. It is very soluble in water, and dissolves in alcohol more readily than cacodylic acid. All its salts either crystallise or form precipitates. It is a dibasic acid, the formula of its normal salts being $As(CH^3)O^3M^2$. The *barium-salt*, prepared as above, crystallises in colourless needles, containing 10 at. of water, which it gives up at 100° C. The anhydrous salt separates as a white powder composed of rhombic crystals, when the concentrated aqueous solution is evaporated or mixed with alcohol. On examining with the microscope the precipitate produced by alcohol, the rhombic crystals are seen to change in a few minutes into the long needles of the hydrated salt. The salt is quite insoluble in alcohol, and may thus be easily separated from cacodylate of barium, which is soluble in that liquid. *Arsenmethylate* of silver, $As(CH^3)O^3Ag^2$, is precipitated in small crystals, having a strong nacreous lustre, on mixing the neutral solution of the barium-salt with nitrate of silver. It is anhydrous, is but little altered by exposure to air and light, does not decompose at 100° C., but explodes at higher temperatures, with rather strong detonation.

Sulphide of Arsenmethyl, $As(CH^3)S$.—Obtained by passing sulphuretted hydrogen into water in which dichloride of arsenmethyl is immersed:

$$As(CH^3)Cl^2 + H^2S = As(CH^3)S + 2HCl.$$

The chloride is then converted into a white mass of the sulphide, without the slightest separation of sulphur. The product is dissolved in a mixture of alcohol and sulphide of carbon, from which it crystallises by rapid evaporation in shining laminæ, or by slow evaporation in small prisms. It is insoluble in water, moderately soluble in alcohol and ether, very soluble in sulphide of carbon. In the crystallised state, it melts at about 100° C., but often remains fluid for a long time after cooling. It is decomposed by heat, with separation of sulphide of arsenic. It is permanent in the air, and has a faint odour like that of asafœtida. The alcoholic solution decomposes the salts of silver, copper, lead, platinum, and mercurosum, with formation of metallic sulphides, and produces a white cloud with mercuric chloride.

ARSENDIMETHYL OR CACODYL. $As(CH^3)^2 = Kd$.—(**Cadet**, Crell. N. Chem. Arch. i. 212; **Bunsen**, Pogg. Ann. xl. 219; xlii. 145; Ann. Ch. Pharm. xxxvii. 6; xlii. 19; **Baeyer**, Ann. Ch. Pharm. cvii. 257.—**Gm.** ix. 316; **Gerh.** i. 626.)—This body, together with the products of its oxidation, constitutes the spontaneously inflammable liquid, known as *Cadet's fuming liquid* or *alkarsin.** To prepare this liquid, a mixture of equal parts of acetate of potassium and arsenious oxide is distilled in a retort provided with a receiver, from which a long tube passes into the chimney, to carry away the poisonous gases evolved during the process. The retort is placed in a sand-bath and gradually heated till it is red-hot at the bottom. A brown oleaginous liquid consisting of impure cacodyl is then found in the receiver, together with metallic arsenic, and a mixture of water, acetone, and acetic acid, which floats on the top. The reaction is very complicated, considerable quantities of carbonic anhydride and hydride of methyl (marsh-gas) being given off, together with other gases in smaller quantity; but the formation of cacodyl is evidently connected with the splitting up of acetic acid at a red heat into carbonic anhydride and hydride of methyl (p. 12). The oily liquid, which is very inflammable, is decanted by means of a syphon, the longer arm of which dips under water. It is then washed with boiled water and distilled over hydrate of potassium in a current of hydrogen.

Pure cacodyl is obtained by decomposing the chloride with metallic zinc, dissolving out the chloride of zinc by water, and dehydrating the oily liquid, which sinks to the bottom, by distillation from chloride of calcium. The strong tendency of cacodyl to take fire in the air and the extremely poisonous quality of its vapour, render it necessary to perform all the distillations in sealed vessels, filled with dry carbonic acid gas. Bunsen's method is as follows:

1. Chloride of cacodyl is prepared perfectly free from oxide, by distilling alkarsin with strong hydrochloric acid, till the resulting chloride no longer emits the slightest fume on exposure to the air; or better, by mixing the dilute alcoholic solutions of alkarsin and mercuric chloride, and distilling the resulting precipitate of *chloromercurate of cacodyl* ($Kd^2O.4HgCl$) with very strong hydrochloric acid. To free the distillate obtained by either of these methods from water and hydrochloric acid, it is digested for several days with a mixture of chloride of calcium and quick lime, contained in the bulb-apparatus A (*fig.* 74). The air is first expelled from this apparatus by a stream of dry carbonic acid gas; the lower extremity *a* is then dipped into the chloride of cacodyl below the hydrochloric acid; the chloride of cacodyl is drawn into the bulb by means of a hand-syringe attached by a caoutchouc tube to the upper end *b*; and lastly the apparatus is sealed at both ends and set aside for several days.

2. The decomposition of the chloride of cacodyl is effected in a second apparatus *B*, represented in *fig.* 75. A moderately strong and rather wide gas-delivery tube is blown out to a bulb in two places *a*, *b*, about six inches apart; the lower extremity is then drawn out and twice bent, as shown at *c*, *d*: the upper bulb *a* is partly filled through the wide open end of the tube with small cuttings of pure zinc-foil; the upper end of the tube is then drawn out and bent, as shown in the figure, and the whole apparatus is filled with perfectly dry carbonic acid gas. To introduce the purified chloride of cacodyl into the bulb *a*, the tube of apparatus *A* is cut off at *c*, just above the bulb; the upper extremity *f* of the apparatus *B*, is then introduced into bulb *A*; and a quantity of the liquid, sufficient to half fill it, is drawn in by means of a hand-syringe connected with the lower end *e*, after which the lower end of the tube is sealed by the blowpipe at *e*, and the upper end sealed and melted off at *g*, close to the bulb *a*. The apparatus is now inverted, and the bulb *a* immersed in water at 100° C. The reduction then takes place without evolution with gas, and after some hours, the contents of the bulb *a* are converted into a white saline mass, which appears to be a compound of cacodyl with chloride of zinc, and melts to an oily liquid at 110°—120° C. To separate the cacodyl from the chloride of zinc, the

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* This liquid was supposed by Bunsen to be the oxide of cacodyl, $(AsC^2H^6)^2O$. It does not appear, however, to be definite in constitution. Bunsen's analyses of it vary from 29·9 to 22·4 per cent. in the carbon, and from 65·4 to 66·2 in the arsenic. Dumas (Ann. Ch. Phys. [3] viii. 362) found 22·0 and 23·2 per cent. carbon, and from 68·9 to 69·3 per cent. arsenic. Now the formula of oxide of cacodyl requires 21·2 carbon, and 66·4 arsenic, while that of cacodyl itself requires 22·9 carbon, and 71·4 arsenic. These results are quite in accordance with the supposition that Cadet's liquid is a variable mixture of cacodyl and its oxide; the spontaneous inflammability of the liquid likewise indicates the presence of free cacodyl. The true oxide of cacodyl (Bunsen's *paracacodylic oxide*, p. 407, supposed by him to be isomeric with alkarsin), produced by slow oxidation of cacodyl or of alkarsin itself, is not spontaneously inflammable. (**Gerhardt.**)

end *e* of the apparatus is broken off under water which has been thoroughly freed from air by boiling; the whole apparatus is heated to expel the carbonic anhydride, and then left to cool, till the bulb *b* is nearly filled with water; the end *e* is again sealed; the apparatus inclined so that the water may flow into the bulb *a*; and this bulb is gently heated. The chloride of zinc then dissolves, and the cacodyl sinks to the bottom as a heavy oily liquid.

Fig. 74.

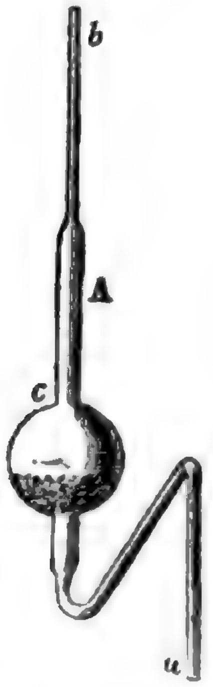
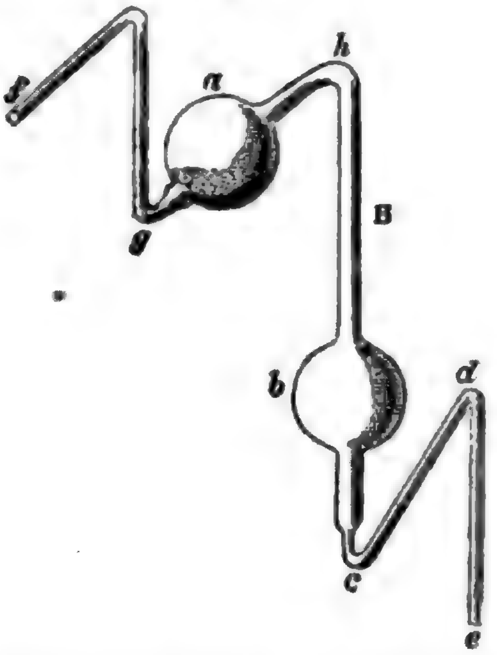


Fig. 75.



To dehydrate the cacodyl and purify it further, it is next transferred, with the same precautions as before, into another apparatus *A* (*fig.* 74), the bulb of which contains dry chloride of calcium: for this purpose, the bulb *a* of apparatus *B* is cut off at *h*, and the apparatus *A* having been filled with dry carbonic acid gas, its lower extremity *a* is introduced into the bulb *a*, and made to dip into the cacodyl below the watery liquid; the cacodyl is then drawn by suction with the syringe into the bulb of apparatus *A*, which is then sealed at both ends, and set aside for some time. The dehydrated cacodyl is next transferred into a second apparatus B, filled with dry carbonic acid gas, and having some zinc-cuttings in the bulb *a*, and the two arms of the tubes are then sealed and melted off just below the bulbs *a*, *b*. The bulb *b* is then immersed in cold water; the cacodyl distilled into it by gently heating the bulb *a* with a spirit-lamp, and then poured back; and the rectification is repeated in this manner two or three times. Lastly, the bulb *b* is cooled in a freezing mixture to −6° C., and left there till about ⅔ of the liquid has crystallised, and the still liquid portion is poured back: that which then remains in the solid state is pure cacodyl.

Cacodyl may also be prepared by heating the sulphide with mercury.

Properties.—Cacodyl is at ordinary temperatures a transparent colourless, strongly refracting liquid, heavier than water. It boils near 170° C. Its vapour-density (referred to air as unity) is by experiment 7·101, which shows that the formula of cacodyl in the free state is $As^2C^4H^{12} = As^2Me^4 = KdKd$. For the atomic weight represented by this formula is 210 ($= 2 . 75 + 4 . 12 + 12 . 1$), and if this represents 2 vols. of vapour, the weight of one vol. of vapour, that is to say, the specific gravity referred to hydrogen as unity, is 105; and multiplying this by 0·0693, the specific gravity of hydrogen referred to air, we obtain for the specific gravity of cacodyl-vapour referred to air as unity, the number 7·2755, which is very near the number determined by experiment. Cacodyl has a disgusting odour, somewhat like that of arsenetted hydrogen, and its vapour is very poisonous. It solidifies at 6° C. in square-based prisms. It is sparingly soluble in water, very soluble in alcohol and in ether. When heated in a close vessel to about 400° C. it is resolved, without deposition of carbon, into metallic arsenic, and a mixture of 2 vol. marsh gas and 1 vol. olefiant gas:

$$As^2C^4H^{12} = 2CH^4 + C^2H^4 + As^2.$$

Cacodyl takes fire in the air, at ordinary temperatures, even more readily than crude alkarsin, yielding carbonic anhydride, water, and arsenious oxide, but if the quantity of air present is not sufficient for complete combustion, a red compound, Bunsen's *erythrarsin*, is formed at the same time. This red substance is also produced when cacodyl is passed through red-hot tubes; also by the action of protochloride of tin, or phosphorous acid on cacodyl. It appears to contain $C^4H^{12}As^4O^3$. Cacodyl exposed to the gradual action of *oxygen*, as when air is passed into it in successive bubbles, is converted first into oxide of cacodyl, and afterwards into cacodylic acid. It takes fire in *chlorine gas*, and is converted by chlorine-water into chloride of cacodyl. It dissolves *sulphur*, forming a protosulphide or trisulphide of cacodyl, according to the quantity. *Fuming sulphuric acid* dissolves it without blackening: the solution gives off, even in the cold, a considerable quantity of sulphurous acid, and yields by distillation a product having an agreeable ethereal odour. It dissolves in *nitric acid*, and the solution yields with *nitrate of silver* a crystalline precipitate of nitrate of silver and cacodyl.

Bromide of Cacodyl, $As(CH^3)^2Br = KdBr$, is obtained by distilling the chloromercurate, $As^2C^4H^{12}O.4HgCl$, with concentrated hydrobromic acid, and is purified like the chloride. It is a yellow liquid, which does not fume in the air, and closely resembles the chloride. When heated over mercury to a temperature between 200° and 300° C. it is decomposed, yielding free cacodyl and mercurous bromide. Heated with water it forms an *oxybromide*.

Chloride of Cacodyl, $As(CH^3)^2Cl = KdCl$.—Prepared by distilling the chloromercurate with very strong hydrochloric acid, and purified from water and adhering hydrochloric acid by placing it in contact with chloride of calcium and quick lime, and distilling it in the hermetically sealed apparatus (*fig.* 74) filled with dry carbonic anhydride. It is also produced by the action of chlorine-water on cacodyl. It is a very mobile liquid, heavier than water, which does not solidify even at $-45°$ C. It boils a little above 100° C., forming a colourless vapour of specific gravity 4·56 (by calculation 4·85). It does not fume in the air, but emits a very pungent intoxicating odour. The vapour mixed with air produces, when inhaled in rather large quantity, swelling of the mucous membrane of the nose and extravasation of blood in the eyes. The vapour evolved from the boiling liquid takes fire spontaneously in the air, and explodes violently when heated with oxygen gas.

Chloride of cacodyl is insoluble in *water* and *ether*, but soluble in all proportions in *alcohol*. *Sulphuric* and *phosphoric acids* decompose it, eliminating hydrochloric acid. Strong *nitric acid* sets it on fire. It burns in *chlorine* gas, with copious deposition of charcoal. *Zinc*, *tin*, and *iron* decompose it, setting the cacodyl free. With *alcoholic potash* it yields chloride of potassium, and an ethereal liquid having a disagreeable odour, and miscible in all proportions with water and alcohol. Mixed with solution of *nitrate of silver*, it gives up the whole of its chlorine, forming a precipitate of chloride of silver.

A *subchloride* or *oxychloride of cacodyl*, $KdCl.xKd^2O$, is obtained by the action of water on the chloride, also by distilling alkarsin with dilute hydrochloric acid, rectifying the product over a mixture of chalk and water, and redistilling in an atmosphere of carbonic anhydride. It is a liquid which resembles the chloride, has a very offensive odour, and boils at 109° C., giving off a vapour of specific gravity 5·46.

Chlorocuprite of Cacodyl, $KdCl.Cu^2Cl$, is obtained as a bulky white precipitate, on mixing an alcoholic solution of chloride of cacodyl with a solution of cuprous chloride in hydrochloric acid. In contact with the air, it turns green, and gives off very fetid arsenical vapours. It is decomposed by heat into its component chlorides.

Chloroplatinate of Cacodyl.—An alcoholic solution of chloride of cacodyl mixed with dichloride of platinum, yields a red-brown precipitate, probably consisting of $AsC^2H^6Cl.PtCl^2$; but on boiling this product with water, a yellow solution is obtained, which on cooling, deposits crystals of a new compound, viz.:

Chloride of Cacoplatyl, $AsC^2H^4PtCl.H^2O$, or rather $AsC^2H^4pt^2Cl.H^2O$, that is to say, the chloride of a radicle, cacoplatyl, formed from cacodyl by the substitution of 2 at. platinicum (pt. = 49·9) for 2 at. hydrogen. It appears to be formed from chloroplatinate of cacodyl, by abstraction of 2HCl. This salt forms needle-shaped crystals, which are inodorous, have a nauseous taste, and are soluble in hot water and alcohol. Ammonia dissolves it in all proportions, and the solution when evaporated yields indistinct crystals insoluble in alcohol. Chloride of cacoplatyl sustains a temperature of 164° C. without decomposing, merely giving off 4 per cent. of water, which it takes up again when boiled with water. At higher temperatures, it turns brown, and then burns away, giving off arsenical vapours and leaving arsenide of platinum. Chloride of cacoplatyl is not attacked by hydrochloric acid; sulphuric acid colours it yellow. With iodide and bromide of potassium, it forms yellow, precipitates of *iodide* and *bromide of cacoplatyl*, precisely similar in composition to the chloride. With nitrate of silver, it forms a precipitate of chloride of silver, the liquid remaining neutral. Boiled with sulphate of silver, it also forms chloride of silver, and the filtered solution evaporated in vacuo yields white crystalline grains of *sulphate of cacoplatyl*, $(AsC^2H^4pt^2)^2.SO^4$. (Gerh. i. 642.)

Trichloride of Cacodyl, $As(CH^3)^2Cl^3$.—Produced: 1. By the action of perchloride of phosphorus on cacodylic acid:

$$KdO^2H + 2PCl^5 = KdCl^3 + 2PCl^3O + HCl.$$

The chloride of phosphorus must be immersed in anhydrous ether, the cacodylic acid in powder added by small portions at a time, and the action moderated by external cooling.—2. By the action of chlorine on the monochloride. The latter compound, when brought directly in contact with chlorine gas, takes fire and undergoes complete decomposition; but if chlorine be led on to the surface of a solution of the monochloride in sulphide of carbon externally cooled, the trichloride is formed in crystalline laminæ, which may be purified by washing with sulphide of carbon.

The trichloride, prepared by the first method, forms beautiful large prismatic crystals, which, however, are very unstable, being instantly decomposed, at temperatures between 40° and 50° C., into chloride of methyl and dichloride of arsen-monomethyl:

$$As(CH^3)^2.Cl^3 = As(CH^3)Cl^2 + CH^3Cl.$$

The decomposition takes place spontaneously in the course of a day at ordinary temperatures, even when the compound is enclosed in sealed tubes. The crystals obtained by the second method are much more stable.

Trichloride of cacodyl dissolves without decomposition in anhydrous ether, and separates by quick cooling of a warm saturated solution, in laminæ, by slow cooling, or spontaneous evaporation, in transparent colourless prisms, which, however, become dull even in a vacuum. It dissolves less freely in sulphide of carbon, from which it separates in large laminæ. Anhydrous alcohol decomposes it, forming a syrup, which, by slow evaporation, yields crystals of basic perchloride of cacodyl, or hydrochlorate of cacodylic acid:

$$As(CH^3)^2Cl^3 + 2(C^2H^5.H.O) = \underbrace{As(CH^3)^2O^2H^2Cl}_{\text{Basic perchloride of cacodyl.}} + \underbrace{2C^2H^5Cl.}_{\text{Chloride of ethyl.}}$$

The alcoholic solution, left to evaporate, gives off a substance, probably *dichloride of arsen-monomethyl* (p. 401), which acts intensely on the mucous membranes. The trichloride fumes in moist air, giving off hydrochloric acid, and forming basic perchloride of cacodyl. The same decomposition takes place in the ethereal solution when exposed to the air, the basic perchloride separating in long needles, the formation of which may be accelerated by the addition of water or alcohol. The trichloride dissolves in water, with considerable rise of temperature, forming a solution of cacodylic acid and hydrochloric acid:

$$As(CH^3)^2Cl^3 + 2H^2O = As(CH^3)^2O^2H + 3HCl.$$

The decomposition is exactly similar to the preceding, the basic perchloride containing indeed the elements of cacodylic and hydrochloric acid:

$$As(CH^3)^2O^2H^2Cl = As(CH^3)^2O^2H + HCl.$$

The ethereal solution of the trichloride does not attack *mercuric oxide;* but on adding alcohol, a brisk action takes place, and an oil separates which contains chlorine and mercury, is soluble in alcohol, and precipitated by ether. On further addition of mercuric oxide, the whole solidifies to a mass of corrosive sublimate, and the compound of that substance with cacodylic acid (p. 408). Oxide of silver is also without action on the ethereal solution. (Baeyer.)

Dibromochloride of Cacodyl, $As(CH^3)^2ClBr^2$.—Bromine acts upon monochloride of cacodyl in the same manner as chlorine. On adding bromine to a mixture of the monochloride and sulphide of carbon, the dibromochloride is precipitated in the form of a yellow crystalline body, which is even more unstable than the trichloride, being quickly resolved into gaseous bromide of methyl, and a liquid which appears to be chlorobromide of arsen-monomethyl, $As(CH^3)^2.ClBr$, but is very unstable. (Baeyer).

Cyanide of Cacodyl, $As(CH^3)^2.CN = KdCy$, is obtained by distilling alkarsin (Cadet's liquor) with strong hydrocyanic acid, or better with a concentrated solution of cyanide of mercury; metallic mercury then separates, and cyanide of cacodyl collects under the water in the receiver, in the form of a yellowish oil, which soon solidifies in fine prismatic crystals. The liquid is decanted, and the crystals are dried by pressure between bibulous paper. The crystals are oblique prisms, truncated on the acute edges, and terminated by dihedral summits. It melts at 33° C., forming a colourless ethereal, strongly refracting liquid, which solidifies again on cooling. It boils at 140° C., yielding a vapour of specific gravity 4·63. It dissolves sparingly in water, much more readily in alcohol and ether. It is intensely poisonous, more so than any other cacodyl-compound. A few grains of it diffused in vapour through the air of a room, are sufficient to excite giddiness, delirium, numbness of the hands and feet, and even loss of consciousness; these attacks, however, are of short duration, provided the person affected make his escape in time. Cyanide of cacodyl is not decomposed by dilute alkalis, but *concentrated acids* decompose it, with evolution of hydrocyanic acid. With *silver-solutions* it forms a precipitate of cyanide of silver. It reduces *mercurous nitrate*, but does not act on mercuric nitrate. With *mercuric chloride*, it forms a white precipitate of chloromercurate of cacodyl.

Fluoride of Cacodyl, $As(CH^3)^2F = KdF$.—Produced by distilling the chloromercurate with hydrofluoric acid. It is a colourless liquid, which has an offensive odour, and attacks glass.

Iodide of Cacodyl, $As(CH^3)^2I = KdI$.—When alkarsin is distilled with concentrated hydriodic acid, an oily liquid passes over, which on cooling deposits transparent rhomboïdal tables, consisting of *oxyiodide of cacodyl*. To complete the separation, the liquid is immersed in a freezing mixture, then decanted from the crystals, and afterwards dried and rectified in the manner described for the chloride, the distillation being, however, discontinued when two-thirds of the liquid have passed over. Iodide of cacodyl thus prepared is a yellowish, slightly syrupy liquid, having a strong repulsive odour. It is heavier than melted chloride of calcium. It remains liquid at −10° C., and boils at a temperature above 100° C.; nevertheless it distils with the vapour of water. It does not fume when exposed to the air, but gradually oxidises and deposits fine prismatic crystals of cacodylic acid. It is soluble in *alcohol* and *ether*, but insoluble in water. *Nitric* and *sulphuric acids* decompose it, setting iodine free. When heated in the air it burns with a dazzling flame, giving off vapours of iodine.

Oxide of Cacodyl, $As^2C^4H^{12}O = Kd^2O$. (Bunsen's *Paracacodylic Oxide*, see p. 403.)—This compound is formed by the slow oxidation of cacodyl; also by the action of reducing agents, such as hydriodic, hydrobromic, sulphydric, or phosphorous acid, protochloride of tin, &c., on cacodylic acid. When air is made to bubble slowly through alkarsin, that liquid is gradually converted into a syrup filled with crystals of cacodylic acid; and on dissolving in water the mass thus obtained, and distilling, water having the odour of cacodyl passes over at first, and afterwards between 120° and 130° C., an oily liquid, which when dried over caustic baryta, and rectified out of contact of air, yields pure oxide of cacodyl, in the form of a limpid oil, having a pungent odour, sparingly soluble in water, and boiling at 120° C. When exposed to the air, it oxidises very slowly, without fuming or rise of temperature, and is converted into cacodylic acid. Air mixed with its vapour between 50° and 70° C. detonates violently on the approach of a burning body. Oxide of cacodyl dissolves in hydrochloric, hydriodic, and hydrobromic acids, forming the chloride, bromide, and iodide of cacodyl.

Oxide of cacodyl forms with *mercuric chloride*, a white precipitate, which is a compound of the two substances $Kd^2O.4HgCl$. This compound, called chloromercurate of cacodyl, is also produced by mixing a dilute alcoholic solution of alkarsin with a dilute solution of mercuric chloride, the latter not being in excess. After several crystallisations from boiling water, it forms silky tufts, and by slow cooling of the solution, may be obtained in small rhombic tables; 100 pts. of boiling water dissolve 3·47 pts. of the compound: it is also soluble in alcohol, especially at the boiling heat. It is inodorous, but has a disagreeable metallic taste, and is very poisonous. When heated in contact with the air, it decomposes without leaving any residue. With hydrochloric, hydriodic, and hydrobromic acids, it forms chloride, iodide, and bromide of cacodyl.

Oxide of cacodyl forms with *mercuric bromide*, a compound similar in composition and properties to that just described, viz. the bromomercurate of cacodyl, $Kd^2O.4HgBr$. With *nitrate of silver*, it forms the compound $3Kd^2O.2NO^3Ag$, which separates in the form of a heavy, white, crystalline powder, on pouring a solution of nitrate of silver into a cold solution of alkarsin in dilute nitric acid. This compound sustains a temperature of 90° C. without decomposing, but explodes at 100° C., giving off fetid arsenical products. With *dichloride of platinum*, oxide of cacodyl forms a red-brown precipitate, and with *cyanide of mercury* a brown pulverulent precipitate, resembling paracyanogen and smelling like dried nightshade berries.

Dioxide of Cacodyl, $AsC^2H^6O = KdO$, or *Cacodylate of Cacodyl*, $\left.\begin{matrix}Kd\\Kd\end{matrix}\right\}O^2$—This is the thick syrupy liquid which is produced by the slow oxidation of cacodyl or alkarsin, and gradually becomes filled with crystals of cacodylic acid. It is decomposed by water, and the liquid then yields a distillate of oxide of cacodyl, and leaves a residue of cacodylic acid:

$$4KdO + H^2O = Kd^2O + 2KdO^2H.$$

Cacodylic Acid, $AsC^2H^7O^2 = KdO^2.H$, or $Kd^2O^3.H^2O$.—This compound may be prepared by passing oxygen gas for several days through alkarsin; the greater part of the liquid is then converted into crystals of cacodylic acid, which may be purified by pressure between paper and recrystallisation. This mode of preparation, however, is disagreeable and dangerous, on account of the inflammability and poisonous character of the cacodyl. A safer and more expeditious method is to oxidise alkarsin with mercuric oxide. The two substances are placed together under water, in a vessel externally cooled; mercury is thereby reduced, and cacodylate of mercury formed:

$$Kd + 2Hg^2O = 3Hg + KdO^2Hg.$$

More alkarsin is then added, drop by drop, till mercury no longer separates on heating the mixture, and a faint odour of cacodyl becomes perceptible; after which the liquid is evaporated, the residue dissolved in alcohol, and the cacodylic acid which crystallises from the solution is purified by recrystallisation from alcohol. It is then obtained in large oblique rhomboidal prisms, transparent and colourless. It is inodorous and not at all poisonous, although it contains 54·35 per cent. of arsenic. It dissolves in water in all proportions, somewhat less freely in alcohol, and is insoluble in ether. It is permanent in dry air, but damp air decomposes it. It is altogether a very stable compound, sustaining a heat of 200° C. without decomposition; at higher temperatures however, it decomposes, yielding arsenious oxide and other arsenical products having a very fetid odour. It is not attacked by fuming nitric acid, or by a mixture of sulphuric acid and chromate of potassium, even at the boiling heat. It is not deoxidised by sulphurous acid, oxalic acid, ferrous sulphate, or hydrogen gas; but when heated with *phosphorous acid*, it gives off vapours of cacodyl. It is also reduced when its aqueous solution is boiled with *zinc*. An acid solution of *protochloride of tin* converts it into chloride of cacodyl. Dry *hydriodic acid* gas, passed over dry cacodylic acid, forms iodide of cacodyl, water, and free iodine:

$$KdO^2H + 3HI = KdI + 2H^2O + 2I.$$

Dry *hydrobromic acid* gas acts in a similar manner. With dry *hydrochloric acid*, on the contrary, or with the concentrated aqueous acid, cacodylic acid unites directly, forming the compound $KdO^2H.ClH$. But by exposing cacodylic acid for some time to a stream of hydrochloric acid gas, *dichloride of arsenmonomethyl* is obtained, together with water and chloride of methyl. (Baeyer):

$$As(CH^3)^2O^2H + 3HCl = AsCH^3Cl^2 + 2H^2O + CH^3Cl.$$

Sulphydric acid, either dry or in aqueous solution, decomposes cacodylic acid, with rise of temperature, forming disulphide of cacodyl, water, and sulphur:

$$2KdO^2H + 3H^2S = 2KdS + 4H^2O + S;$$

but if the cacodylic acid is dissolved in weak alcohol, a considerable quantity of protosulphide is formed as well as disulphide:

$$2KdO^2H + 3H^2S = Kd^2S + 4H^2O + 2S.$$

Cacodylates.—Cacodylic acid dissolves metallic oxides, and decomposes carbonates with effervescence. Most of its salts are gummy, but few being capable of crystallising. The general formula of the normal cacodylates is $AsC^2H^6MO^2 = KdO^2M$. They require a higher temperature to decompose them than the acid, and give off stinking products, leaving a residue of carbonate or arsenate. They dissolve in water and in alcohol. Sulphydric acid converts them into the corresponding *sulpho-cacodylates* KdS^2M. With *silver*, cacodylic acid forms a normal salt, KdO^4Ag, and an acid salt, $KdO^2Ag.2KdO^2H$, both of which crystallise in needles.

Cacodylic acid also combines with certain *acids*.

Hydrochlorate of cacodylic acid, $KdO^2H.ClH$, called by Bunsen, *basic perchloride of cacodyl*, is obtained by dissolving cacodylic acid in concentrated hydrochloric acid, and evaporating in vacuo. It then solidifies in a mass of beautiful lamellated crystals, inodorous, but having a strong acid taste (Bunsen). It is also produced by the action of water or alcohol on trichloride of cacodyl (Baeyer, p. 406). The compound is decomposed by water into hydrochloric and cacodylic acids, and when heated to 200° C. gives off monochlorinated hydride of methyl, water, hydrochloric acid, and an oily liquid, leaving a residue of arsenious acid.

On mixing the alcoholic solutions of cacodylic acid and mercuric chloride, a *cacodylate of mercuric chloride*, $Kd^2O^4.2HgCl$, is precipitated in white shining scales, which change after a while to slender needles.

Hydrofluoric acid forms with cacodylic acid a similar compound, $KdO^2H.FH$, which crystallises in fine prisms. *Hydrobromic acid* also unites directly with cacodylic acid, but the compound is a syrupy liquid which does not crystallise.

Selenide of Cacodyl, is obtained by distilling chloride of cacodyl two or three times with aqueous selenide of sodium. It passes over with the vapour of water, in the form of a heavy yellow oil, having an extremely offensive odour. It is insoluble in water, but soluble in alcohol and ether. It has a very high boiling point. It forms black precipitates with *lead* and *silver* salts, and with *mercuric chloride*, it yields first a black precipitate of sulphide of mercury, and afterwards, on further addition of the mercury-salt, a copious precipitate of chloromercurate of cacodyl.

Sulphide of Cacodyl, $As^2C^4H^{12}S = Kd^2S$, may be prepared by adding a solution of sulphide of barium to the crude liquid obtained by distilling acetate of potassium with arsenious oxide, or by distilling sulphydrate of barium with chloride of cacodyl. It is purified by means of carbonate of lead and chloride of calcium. It is a transparent, colourless, extremely fetid liquid, which retains its fluidity at 40° C., and boils at a temperature considerably above 100°, yielding a vapour of specific gravity 7·72. It is nearly insoluble in water, but mixes in all proportions with alcohol and ether. It does not fume in the air, but rapidly absorbs oxygen, being converted into dioxide and disulphide of cacodyl:

$$Kd^2S + O = KdO + KdS.$$

Hydrochloric acid converts it into chloride of cacodyl, with evolution of sulphydric acid.

Disulphide of Cacodyl, KdS, or *Sulphocacodylate of cacodyl*, $\left.\begin{matrix}Kd\\Kd\end{matrix}\right\}S^2$.—Obtained by the action of sulphur on cacodyl, or on the monosulphides, or by treating cacodylic acid with sulphuretted hydrogen in a vessel externally cooled. Disulphide of cacodyl then separates, mixed with excess of sulphur, from which it may be separated by solution in boiling alcohol. The solution, if slowly cooled, deposits the disulphide in large rhombic tables, but if quickly cooled, in small prisms, soft and greasy to the touch. The compound has a pungent odour, like that of asafœtida, is permanent in the air, and melts at 50° C., forming a colourless liquid, which solidifies in a crystalline mass on cooling. It is insoluble in water, but dissolves readily in alcohol, very sparingly in ether. It dissolves in hydrochloric acid without alteration; in strong sulphuric acid, with evolution of sulphurous acid and separation of sulphur. Nitric acid and peroxide of lead convert it into cacodylic acid. Mercury decomposes it, forming protosulphide of cacodyl, and sulphide of mercury.

Sulphocacodylic acid, $AsC^2H^6S^2 = KdS^2H$.—This acid has not been obtained in the free state, but its salts, KdS^2M, are obtained by precipitating the alcoholic solution of the disulphide with alcoholic solutions of certain metallic salts, or by decomposing the cacodylates with sulphydric acid. The *lead-salt*, KdS^2Pb, forms small white pearly scales, which are indorous, permanent in the air, not affected by sulphydric acid, insoluble in water, nearly insoluble in alcohol. The *cuprous salt*, KdS^2Ccu, [$Ccu = Cu^2$], is obtained by adding an alcoholic solution of cupric nitrate to a large excess of alcoholic disulphide of cacodyl, cacodylic acid and nitrate of cacodyl being formed at the same time:

$$4KdS + 2NO^3Cu + 2H^2O = 2KdS^2Cu + KdO^2H + NO^3Kd + NO^3H.$$

It is a soft, loose, egg-yellow powder, which is decomposed by heat, and is insoluble in water, aqueous acids, alcohol, and ether. The *antimony-salt*, Kd^3S^6Sb (Sb being equivalent to H^3), crystallises in short light yellow needles, difficult to purify. The *bismuth-salt*, Kd^3S^6Bi, forms delicate, golden-yellow, inodorous scales, which are permanent in the air, sustain a heat of 100° C. without decomposition, and are not affected by sulphydric acid. They are insoluble in water, and nearly insoluble in alcohol and ether. The *gold-salt*, KdS^2Au, is obtained by mixing the alcoholic solutions of disulphide of cacodyl and trichloride of gold, cacodylic acid being formed at the same time, as a soft, yellowish white, tasteless, inodorous powder, which is set on fire by strong nitric acid, with separation of sulphur and gold. It is decomposed by caustic potash, but not by sulphydric acid. Insoluble in water, hydrochloric acid, alcohol and ether.

ARSENTRIMETHYL $As(CH^3)^3$ and **ARSENMETHYLIUM** $As(CH^3)^4$. (**Cahours** and **Riche**, Compt. rend. xxxix. 541.)—When iodide of methyl is dropped by small portions into a small flask filled with carbonic anhydride and containing pulverised arsenide of sodium, a considerable degree of heat is developed; and if the additions of iodide of methyl be repeated till no further rise of temperature is produced, and the mixture be then distilled in a current of carbonic anhydride, four products are obtained, viz. unaltered iodide of methyl, a white crystalline body, and a heavy liquid composed of two distinct compounds, one of which boils at 120° C., the other between 165 and 170°. The former is arsentrimethyl; the latter arsendimethyl or cacodyl. The quantity of these liquids obtained is but small, even when the matter operated upon amounts to 100 grammes.

Arsentrimethyl is obtained pure by the decomposition of iodide of arsenmethylium, *e.g.* by treating the compound of iodide of arsenmethylium and iodide of arsenic (*vid. inf.*) with boiling potash-ley, evaporating to dryness, and distilling in an atmosphere of carbonic anhydride. It is a colourless mobile liquid, boiling below 100° C. It is diatomic. The *oxide*, $AsMe^3O$, is crystallisable but deliquescent. The *sulphide*, $AsMe^3S$ crystallises from aqueous or alcoholic solution by slow evaporation in colourless prisms. It unites already with iodine and bromine, forming the compounds $AsMe^3I^2$ and $AsMe^3Br^2$. (Cahours, Compt. rend. xlix 87; Jahresber. d. Chem. 1859, 431.)

Iodide of Arsenmethylium.—This is the crystallised body just mentioned, which is in fact the chief product of the reaction. It may also be obtained by the action of iodide of methyl upon cacodyl. On mixing these two liquids in a tube, a violent action takes place, and a yellowish white mass of crystals of iodide of arsenmethylium is obtained, impregnated with an oily matter of the same colour, consisting of iodide of cacodyl:

$$2CH^3I + 2As(CH^3)^2 = As(C^2H^3)^4I + AsC^2H^6.I.$$

The crystals, freed from the oil by draining and pressure between bibulous paper, and then dissolved in iodide of methyl mixed with alcohol, separate from the solution in the form of beautiful colourless tables having a high lustre.

Iodide of arsenmethylium boiled with recently precipitated oxide of silver, yields a strongly alkaline liquid, which, when evaporated in vacuo, yields very deliquescent crystalline laminæ consisting of the *hydrated oxide of arsenmethylium;* and its solution mixed with sulphate or nitrate of silver, yields iodide of silver, and *sulphate* of arsenmethylium, $SO^4(AsMe^4)^2$, or the *nitrate*, NO^3AsMe^4. These salts are very soluble, highly deliquescent, and separate from their solutions by evaporation in vacuo, in the form of beautiful crystals.

Iodide of Arsenmethylium with Tri-iodide of Arsènic $As(CH^3)^4I.AsI^3$.—When iodide of methyl is heated to 200° C., in contact with metallic arsenic, the latter disappears, and a large quantity of orange-red tabular crystals are obtained, moistened with a brownish liquid.

The crystals are decomposed by distillation, yielding an oil which has a penetrating odour and excites tears. This oil is a mixture of several substances, the least volatile of which boils at 170° C., has the composition of iodide of cacodyl, and yields cacodyl when distilled with amalgam of zinc; the more volatile portion deposits long white very beautiful needles, isomeric with iodide of cacodyl.

Iodide of Arsenmethylium and Zinc, $As(CH^3)^4I.ZnI$, is obtained in colourless crystals by heating iodide of methyl with arsenide of zinc. It is decomposed by boiling with potash-ley, a heavy oil separating, which solidifies on cooling, and if this mass be exposed to the air till the free potash is converted into carbonate, then exhausted with absolute alcohol, and the alcohol left to evaporate, iodide of arsenmethylium crystallises out in prisms. (Cahours, Compt. rend. xlix. 87.)

Iodide of Arsenmethylium and Cadmium, $As(CH^3)^4I.CdI$, is obtained in like manner and exhibits similar properties. (Cahours.)

Tri-iodide of Arsenmethylium, $As(CH^3)^4I^3$.—Analogous to tri-iodide of tetrethylium. (Cahours.)

Bromide of Arsenmethylium.—Bromide of methyl acts energetically on cacodyl, yielding bromide of arsenmethylium in beautiful, very deliquescent crystals, and liquid bromide of cacodyl. (Cahours and Riche.)

ARSENDIMETHYL-DIETHYLIUM. $As(CH^3)^2(C^2H^5)^2 = AsMe^2E^2$.—(Cahours and Riche, Compt. rend xxxix. 544.)

This radicle, like the preceding, has not been obtained in the free state, but the sulphide, iodide, bromide, and chloride are formed, together with the corresponding compounds of cacodyl, by the action of sulphide, iodide, &c., of ethyl on cacodyl.

Iodide. $As(CH^3)^2(C^2H^5)^2I$.—When iodide of ethyl is mixed with cacodyl, no apparent change takes place at first; but the mixture, when left to itself, gradually deposits magnificent crystals of iodide of arsendimethyldiethylium, and likewise yields an oil consisting of iodide of cacodyl:

$$2EI + 2AsMe^2 = AsMe^2E^2I + AsMe^2I.$$

Bromide and *Chloride of ethyl* act in a similar manner, but more slowly. To obtain *chloride of arsenmethethylium*, the mixture must be heated in sealed tubes to 180° or 200° C.; it then deposits an oil containing needle-shaped crystals of the chloride. On distilling the oil and leaving the distillate to cool, these crystals separate in large quantity. Chloride of arsendimethyldiethylium forms crystalline compounds with chloride of mercury, trichloride of gold, and dichloride of platinum.

The *Hydrate* is formed by treating a solution of the iodide with oxide of silver; a strongly alkaline liquid is then obtained, which, when evaporated, deposits the oxide in very deliquescent crystalline scales.

Sulphide.—Sulphide of ethyl acts very slowly on cacodyl, and only when heated, forming crystalline sulphide of arsendimethyldiethylium and a yellowish oil, consisting of sulphide of cacodyl.

The *Sulphate* and *Nitrate* are obtained in the form of very deliquescent crystals, by treating the solution of the iodide with sulphate or nitrate of silver.

ARSENTRIMETHYL-ETHYLIUM, $AsMe^3EI$, and ARSENMETHYL-TRIETHYLIUM, $AsMeE^3$.—The iodides of these radicles are obtained by treating arsentrimethyl with iodide of ethyl, and arsentriethyl with iodide of methyl respectively. Both are isomorphous with the iodides of arsentetramethylium and arsentetrethylium.

ARSENDIMETHYL-DIAMYLIUM, $As(C^2H^3)^2(C^5H^{11})^2 = AsMe^2Am^2$.—The iodide of this radicle is produced, together with iodide of cacodyl, by heating cacodyl with iodide of amyl to 180° C. for two or three days. It crystallises either in nacreous needles, or in thin plates. Treated with oxide, nitrate, and sulphate of silver, it yields the *oxide*, *nitrate*, and *sulphate* of arsendimethyldiamylium. (Cahours and Riche.)

The arsenides of methyl and their compounds are related to one another by the following law. If we arrange them in two groups, the one formed on the type of chloride of ammonium, NH^4Cl, the other on that of ammonia, NH^3, as in the following tables, we find that each member of the second column may be derived from the one next above it in the first, by abstraction of chloride of methyl; and each member in the first column except the highest, may be formed from the one next above it in the second, by addition of 2 atoms of chlorine, the series extending from chloride of arsentetramethylium to trichloride of arsenic:

Type NH^4Cl.	*Type* NH^3.
As Me Me Me Me Cl	
	As Me Me Me
As Me Me Me Cl Cl	
	As Me Me Cl
As Me Me Cl Cl Cl	
	As Me Cl Cl
As Me Cl Cl Cl Cl	
	As Cl Cl Cl

All the reactions indicated in this table have been actually observed, excepting the resolution of $AsMe^4Cl$ into $AsMe^3$ and $MeCl$, and that of $AsMe^3Cl^2$ into $AsMe^2Cl$ and $MeCl$; but a decomposition analogous to the former of these, appears to take place in the preparation of the iodides of the arsenmethyls and arsenethyls, the iodide of arsenmethylium or arsenethylium being formed at first, and then resolved by distillation into iodide of methyl or ethyl, and arsentrimethyl or arsentriethyl, just as iodide of tetrethylium, $N(C^2H^5)^4I$, is resolved under similar circumstances into iodide of ethyl and triethylamine.

There is also another relation to be observed between these compounds, viz. that each of them may be derived from the one immediately above it in the same column, by substitution of chlorine for methyl; and hence it appears that $AsMe^4$ is monatomic; $AsMe^3$ diatomic; $AsMe^2$ either monatomic or triatomic; and $AsMe$ either diatomic or tetratomic; just as in chloride of propyl, C^3H^7Cl, the radicle C^3H^7 replaces 1 at. hydrogen, whereas in chloride of propylene, $C^3H^6Cl^2$, derived from the former by substitution of 1Cl for 1H, the radicle C^3H^6 takes the place of 2 atoms of hydrogen; and in trichlorhydrin, $C^3H^5Cl^3$, the next term in the same series, C^3H^5 (glyceryl), takes the place of 3 at. H. Moreover, just as the group C^3H^5 is monatomic in the allyl-compounds, and triatomic in the glyceryl-compounds, so likewise $As(CH^3)^2$ is sometimes monatomic and sometimes triatomic. The analogy between the two series of compounds will be more clearly seen from the following tabular view:

$As(\overset{\prime}{C}H^3)^2 \ . \ Cl$	$\overset{\prime}{C^3}H^7 \ . \ Cl$
$As(\overset{\prime\prime}{C}H^3)^3 \ . \ Cl^2$	$\overset{\prime\prime}{C^3}H^6 \ . \ Cl^2$
$As(\overset{\prime\prime\prime}{C}H^3)^2 \ . \ Cl^3$	$\overset{\prime\prime\prime}{C^3}H^5 \ . \ Cl^3$
$As(\overset{\prime}{C}H^3)^2 \quad Cl.$	$\overset{\prime}{C^3}H^5 \ . \ Cl.$

Similar analogies may be traced in the compounds of arsenic and ethyl, and likewise, though not yet quite so clearly, in the compounds of antimony, bismuth, and phosphorus, with the alcohol-radicles. (Baeyer.)—In fact, the compounds of these metalloïdal radicles may, in almost all cases, be reduced to the general types MR^3 M^2R^3, MR^5, M^2R^5, where M stands for P, As, Sb, or Bi; and the 3 or 5 at. R are made up, partly by an alcohol-radicle, partly by an equivalent quantity of chlorine, iodine, oxygen, sulphur, &c. (See ORGANO-METALLIC BODIES.)

Arsenide of Tetryl. *Tetryl- or Butyl-cacodyl. Cacodyl of Valeric Acid.*—When valerate of potassium is distilled with an equal weight of arsenious oxide, a heavy yellowish oil passes over, which has a penetrating alliaceous odour, fumes copiously in the air, but does not take fire spontaneously. It is soluble in water, forms a thick white precipitate with mercuric chloride, and appears to reduce mercuric oxide to the metallic state. When left for some time in a loosely closed vessel, it changes entirely into a mass of large, hard, shining, nearly colourless, prisms, which, after drying between filtering paper, are destitute of odour. They have an acid reaction, dissolve in water, and are completely decomposed by nitrate of silver. (Gibbs, Sill. Am. J. [2] xv. 118.)

Arsenide of Trityl. *Trityl- or Propyl-cacodyl. Cacodyl of Butyric Acid.*—By distilling equal weights of butyrate of calcium and arsenious oxide, shaking up the distillate with magnesia and water, and rectifying, a heavy colourless oily liquid is obtained, which has a disgusting cacodyl-odour, does not fume in the air, but burns when set on fire with a white flame and arsenical smoke. The watery liquid which passes over with the oil, appears to contain a considerable quantity of it, and gives a white precipitate with mercuric chloride, the cacodyl-odour being at the same time destroyed. The precipitate dissolves on heating the liquid, but reappears in small crystals on cooling. On mixing the solution and the crystals with hydrochloric acid and zinc, the odour of cacodyl reappears, the evolved hydrogen gives off thick white fumes in the air, and deposits an orange-coloured substance on cold bodies. The mixture when heated yields a colourless fœtid oil, which fumes in the air, but is not spontaneously inflammable. (Wöhler, Ann. Ch. Pharm. lxviii. 127.)

ARSENIOSIDERITE. *Arsenocrocite.* A hydrated ferrico-calcite arsenate, occurring at Romanèche, near Macon, in spherical masses of fibrous texture and yellow colour. Its exact composition has not been determined.

ARSENITE or **ARSENOLITE.** *Arsenic bloom. Native Arsenious Oxide.*—A rare mineral, generally occurring in needle-shaped or capillary crystals, also massive, with spherical and botryoïdal surface; very rarely in regular octahedrons. Specific gravity = 3·69 to 3·71. Hardness = 1·5. It consists of arsenious oxide more or less pure, has a white to greyish-white colour, occasionally yellow, red, or green; sometimes covered with a blackish crust (? suboxide or a mixture of arsenious oxide with metallic arsenic). It is translucent, with vitreous to silky lustre. It is found, accompanying ores of silver, lead, arsenical iron, cobalt, nickel, &c., at Andreasburg in the Harz; also at Joachimsthal in Bohemia, Kapnik in Hungary, and in the old mines of Biber in Hanau. (Dana, ii. 139.)

ARSENOMELANE. See BINNITE.

ARSENOPYRITE. Syn. with MISPICKEL.

ARSENOSIDERITE. Native diarsenide of iron. (See IRON, ARSENIDES OF.)

ARSENPHYLLITE. Breithaupt's name for a mineral which, according to him, has the composition of arsenious oxide, but crystallises in forms of the trimetric system, isomorphous with valentinite. The trioxides of arsenic and antimony are therefore isodimorphous.

ARSIDOGEN. The name given by L. Gmelin (Handb. ix. 315), to the hypothetical compound AsH^2 (= Ar), analogous to amidogen, NH^2, formerly supposed by Laurent, Gerhardt, and Dumas, to exist in cacodyl and its derivatives. According to this view, cacodyl was supposed to be the hydride of a compound, C^4ArH^3, analogous to ethylene, viz. $C^4ArH^3.H$; oxide of cacodyl = $C^4ArH^3.HO$; the protosulphide = $C^4ArH^3.HS$, &c.

ARTHANITIN, or **CYCLAMIN,** a crystalline substance extracted by Saladin (J. Chim. méd. vi. 417), from the roots of *Cyclamen Europæum* (*Arthanita officinalis*).—It is said also to exist in small quantity in the roots of the cowslip (*Primula veris*), of *Anagallis arvensis*, and *Limosella aquatica*.—It is prepared by digesting the fresh roots of cyclamen with alcohol, evaporating the extract, and treating the residue, first with ether, then with cold water: the insoluble part constitutes arthanitin. It is purified by recrystallisation from alcohol, with the aid of animal charcoal. It crystallises in fine colourless needles, which are inodorous, but have a strongly acrid and styptic taste. It is neutral to vegetable colours, dissolves in 500 pts. of water, readily in alcohol. It is altered at the temperature of boiling water, becoming less soluble in alcohol. Nitric acid transforms it into oxalic acid. Sulphuric acid communicates to it a violet-red tint. Taken internally, arthanitin acts like a purgative, and produces vomiting.

ARTICHOKE. According to Verdeil (Compt. rend. xli. 588), the green colouring matter of the artichoke (*Cynara scolymus*) and other composite plants, is a substance distinct from chlorophyll, and is formed by the action of the air, water, and ammonia, on the comminuted parts of the plants. The liquid, which has a fine green colour, forms with acetic acid a bulky green precipitate, which resembles indigo when dry, but when treated with aqueous alkalis, again forms solutions of a beautiful green colour.

The artichoke yields, according to Richardson (Ann. Ch. Pharm. lxvii. Table), in the fresh state, 1·17 per cent. of ash; in the dry state, 6·2 per cent. In the roots, stems, and leaves of the Jerusalem artichoke (*Helianthus tuberosus*) Way and Ogston (Journ. of Agric. Soc. vii. [2] 593) found in the fresh state, 1·79, 1·94, and 15·00 per cent. of ash; in the same parts when dried, 12·2, 4·4, and 28·3 per cent. The constituents of the ash are given in the following table:

	Artichoke.	Jerusalem Artichoke.		
		Root.	Stem.	Leaves.
Potash	24·0	55·9	38·4	6·8
Soda	5·5		0·7	3·7
Lime	9·6	3·3	20·3	40·1
Magnesia	4·1	1·3	1·9	2·0
Sulphuric acid (SO^3)	5·2	3·8	3·2	2·0
Carbonic acid (CO^2)		11·8	25·4	24·3
Phosphoric acid (P^2O^5)	36 2	16·7	3 0	0·6
Silica	7·0	1·5	1·5	17·5
Sesquioxide of iron		0 5	0·9	1·1
Chloride of potassium		5·0		
Chloride of sodium	3·6		4·7	1·8
Sesquiphosphate of iron	4·8			

ARTOCARPUS INCISA. The fruit of this tree, the bread-fruit tree, which grows in the islands of the East Indian Archipelago, contains 14 per cent. of starch, 3 per cent. albumin, 19 gluten and woody fibre, and 63 water.

ARUM ESCULENTUM. The fresh tubers of this plant yield, according to T. J. Herapath (Chem. Soc. Qu. J. iii. 193), 1·65 per cent. ash, containing in 100 pts.: 61·7 pts. soluble in water, and consisting of 45·1 K^2O; 8·1 NaCl; 3·8 SO^3; 4·7 P^2O^5; and 38·7 pts. insoluble in water, consisting of 18·3 K^2O; 1·1 Fe^4O^3; 11·4 P^2O^5, 6·1 SiO^2.

ARUM MACULATUM. The fresh plant contains a sharp milky juice, which produces inflammation of the skin, but is so volatile and unstable that it is no longer present in the dried root. The dry root is said to contain 71 per cent. starch, together with 23 per cent. gum and vegetable mucus.

ARUNDO PHRAGMITES. The dry plant yields 4·7 per cent. of ash, which according to Schulz-Fleeth (Pogg. Ann. lxxxiv. 80), contains in 100 pts.: 8·6 K^2O; 5·9 Ca^2O; 1·2 Mg^2O; 0·2 Fe^4O^3; 2·8 SO^3; 71·5 SiO^2; 6·6 CO^2; 2·0 P^2O^5; 0·4 NaCl.

ASA DULCIS. See Benzoin.

ASAFŒTIDA. *Gummi Asæ fœtidæ, Stinkasant, Teufelsdreck.*—A gum-resin extracted from the root of the *Ferula Asafœtida*, an umbelliferous plant growing in Persia. The root, which is black on the outer surface, resembles a large parsnep. On cutting it transversely, the asafœtida exudes in the form of a white juice, like cream, but on exposure to the air, it gradually becomes yellow and at last dark brown. It is very apt to run into decomposition; hence, those who collect it carefully defend it from the sun. The fresh juice has an excessively strong smell, which grows weaker and weaker upon keeping; a single dram of the fresh fluid smells more than a hundred pounds of the dry asafœtida brought to us. The Persians are commonly obliged to hire ships on purpose for its carriage, as scarcely any one will receive it along with other commodities, its stench infecting everything that comes near it.

Asafœtida is met with, sometimes in small drops or tears, but more frequently in reddish masses with white streaks. Specific gravity 1·327. Its recently fractured surface has but little colour, but quickly reddens on exposure to the air. It is friable at very low temperatures, but softens at the heat of the hand. It dissolves in alcohol much more readily than in water. It has an extremely disagreeable alliaceous odour, and a sharp biting taste. It contains in 100 pts., according to Pelletier (Bull. Pharm. iii. 556), 65·0 of resin, 19·4 soluble gum, 11·2 bassorin, 3·6 volatile oil, and 0·3 of malate of calcium. According to Johnston (Phil. Mag. Dec. 1838) the resin of asafœtida, which may be extracted by alcohol, is of a light yellow colour, when pure, but becomes purple on exposure to the sun. It contains about 70·2 per cent. of carbon, 7·6 of hydrogen, and 22·2 of oxygen; no sulphur. Asafœtida is used as a remedy in nervous and hysteric affections, as a deobstruent, and sometimes as an anthelmintic. It is said to be used also by some Asiatic tribes as a condiment.

Oil of Asafœtida.—Asafœtida distilled with water yields about 3 per cent. of a sulphuretted essential oil, to which its odour is due. This oil is neutral, begins to boil between 135° and 140° C., and when left at rest, gives off a considerable quantity of sulphydric acid. Hlasiwetz (Ann. Ch. Pharm. lxxi. 23) obtained from it by analysis, from 64·2 to 69·3 per cent. carbon, from 9·1 to 10·5 per cent. hydrogen, and 20·2 to 25·5 per cent. sulphur, its composition varying with the time elapsed since its preparation. Hlasiwetz regards it as a variable mixture of the two compounds $C^{12}H^{22}S^4$ and $C^{12}H^{22}S$. When it is treated with oxide of silver, sulphide of silver is formed, and the liquid, if afterwards rectified, contains 65·6 per cent. C, 13·1 H, and 24·8 S. On agitating it with strong solution of potash and hydrate of lead, and then rectifying, an oil is obtained having an odour of lavender or rosemary, and containing about 60·7 per cent. C, 9·5 N, and 29·85 S. An oil having the same composition is obtained by passing sulphurous acid gas through the crude oil.

The alcoholic solution of oil of asafœtida forms with dichloride of platinum, yellow or brown precipitates varying in composition, according to the strength of the solutions and the duration of the action, but all containing the same proportions of carbon and hydrogen as the oil itself, viz. C^6H^{11}.

On mixing concentrated alcoholic solutions of oil of asafœtida and chloride of mercury a white precipitate is formed, which is partly dissolved by boiling alcohol; and the solution on cooling yields microscopic crystals containing $2C^6H^{11}S.5Hg^2S + 2C^6H^{11}Cl^2.HgCl$. The portion of the precipitate insoluble in alcohol, blackens when treated with potash, a proof that it contains mercurous chloride: it was found to contain $C^6H^{11}S^4.Hg^2S.4Hg^2Cl.4Hg^2SCl$. Both these mercury-compounds, when treated with sulphocyanate of potassium, yield a volatile oil smelling like oil of mustard, and like that oil, forming a crystalline compound with ammonia: it does not however contain allyl, but probably the homologous radicle, C^6H^{11} (Hlasiwetz, Hand. d. Chem. 2^{te} Aufl. ii. 339.)

ASARIN or **ASARONE**, $C^{20}H^{26}O^5$.—This substance is contained in the root of asarabacca (*Asarum europæum*) and passes over in the crystalline form when the dry root is distilled with water. The crystals belong to the monoclinic or oblique prismatic system, and resemble camphor in taste and odour. Asarone melts at 40° C., begins to boil at 280°, and may be sublimed in small quantity between two watch-glasses. It is insoluble in water, but dissolves readily in alcohol, ether, and essential oils. When it is boiled for some time with alcohol, the solution gradually turns red, and a portion of the asarone is converted into an uncrystallisable, resinous, isomeric modfication, which does not distil with vapour of water, and decomposes at 300° C. Nitric acid converts asarone into oxalic acid. It is dissolved with red colour by strong sulphuric acid, and reprecipitated by water. It is strongly attacked by chlorine, giving off hydrochloric acid, and yielding a thick oil whose composition approximates to the formula $C^{20}H^{22}Cl^4O^5$. (Goertz, Pfaff's System d. Materia Medica, iv. 229; Blanchet and Sell, Ann. Ch. Pharm. vi. 296; Schmidt, *ibid.* liii. 156.)

ASARITE. A camphor-like substance found, together with asarone, in the root of *Asarum europuæm*, and resembling that substance in many respects, but differing from it in appearance, in not decomposing so readily when sublimed, but chiefly in its melting point which is 70° C. whereas that of asarone is 40°. It is obtained by dissolving in alcohol the impure crystals of asarone as they are obtained by distilling the root with water, precipitating by alcohol, and collecting the small silky crystals which float about in the liquid. Gräger, who obtained this substance at first, regarded it as a distinct body, but was afterwards disposed to regard it as identical with asarone: the difference in the melting point is, however, too great to be accounted for by error of observation. Blanchet and Sell suppose it to be the solid part of asurum-oil, and asarone a product of the decomposition of that oil.

ASARUM-OIL. A volatile oil existing in small quantity (about $\frac{1}{180}$) in the root of *Asarum europæum*, and passing over, together with asarone, when the root is distilled with water. It may be separated from the asarone by treating the oily portion of the distillate with a small quantity of alcohol. Two layers then form, the upper being an alcoholic solution of asarone, containing a little of the oil; the lower, a solution of small quantities of asarone and alcohol in the oil. On distilling this lower liquid over hydrate of lime, and leaving the distillate to stand for some time, the asarone separates out, and the remaining oil may be dehydrated by chloride of calcium. The oil is yellowish and viscid, smells like valerian oil, has a sharp burning taste, is lighter than water, sparingly soluble in water, but easily soluble in alcohol, ether, and in oils both fat and volatile. Blanchet and Sell (Ann. Ch. Pharm. vi. 296) deduce from their analysis (74·4 C, and 9·7 H) the formula C^8H^9O, which does not agree very well with it: the formula $C^{10}H^{15}O^2$, is more in accordance with the analysis. As, however, the oil doubtless still contained asarone, it is useless to attempt to determine its formula exactly till further experiments are made. It appears, however, to contain more carbon and hydrogen than asarone, which therefore may have been formed from it by oxidation.

ASBESTOS, or **ASBESTUS.** (ἄσβεστος, indestructible.)—A mineralogical term used rather to denote a peculiar form assumed by several minerals, than to designate any particular species. It is, in fact, applied to several varieties of amphibolic and augitic minerals, such as *actinolite*, *tremolite*, *anthophyllite*, &c. which occur in long capillary crystals, placed side by side in a parallel position, thus producing a fibrous mass. These conditions may be fulfilled in various degeees, and there are accordingly various kinds of asbestos. Those varieties whose fibres are very delicately and regularly arranged, are called *flexible asbestos*, or *amianth* (a Greek term, signifying *unpolluted*); the individual crystals are easily separated from each other, are very flexible and elastic, and have a white or greenish colour, with a fine silky lustre. A single fibre of this mineral fuses readily into a white enamel; but in the mass, it is capable of resisting ordinary flame, so that when woven it produces a fire-proof cloth. The most beautiful specimens are found in the Tarantaise in Savoy, and in Corsica, where it occurs very abundantly. It is also found near Barège in the Pyrenees, in Dauphiny, and on the St. Gothard; at St. Neverne in Cornwall; at Portsoy in Scotland; in mica slate at Glenelg, Inverness-shire; and near Durham. Those varieties in which the crystals are coarser, with scarcely any flexibility, are called *common asbestos*. There are also three other varieties, called *mountain leather*, *mountain cork*, and *mountain wood*, which differ from common asbestos by the fibres interlacing each other.

Common asbestos occurs in masses of fibres of a dull greenish colour, and of a somewhat pearly lustre. Fragments splintery. It is scarcely flexible, and much denser than amianthus. It is slightly unctuous to the touch. Specific gravity 2·7. Fuses with difficulty into a greyish-black scoria. It is more abundant than amianthus, and is found usually in serpentine, as at Portsoy in the Isle of Anglesea, and at the Lizard in Cornwall. It was found in the limestone of Glentilt, by Dr. M'Culloch, in a pasty state, but soon hardened by exposure to air.

Mountain Leather consists, not of parallel fibres like the preceding, but interwoven and interlaced so as to become tough. When in very thin pieces, it is called *mountain paper*. Its colour is yellowish-white, and its touch meagre. It is found at Wanlockhead, in Lanarkshire. Its specific gravity is uncertain.

Mountain Cork, or *Elastic Asbestos*, is, like the preceding, of an interlaced fibrous texture; opaque; has a meagre feel and appearance, not unlike common cork, and like that substance is somewhat elastic. It floats on water. Its colours are, white, grey, and yellowish-brown. It takes an impression from the nail; is very tough; cracks when handled, and melts with difficulty before the blowpipe. Specific gravity from 0·68 to 0·99.

Mountain Wood.—Ligniform asbestos is usually massive, of a brown colour, and has the aspect of wood. Internal lustre glimmering. Soft, sectile, and tough; opaque; feels meagre; melts to a black slag. Specific gravity 2·0. It is found in the Tyrol; Dauphiny; and in Scotland, at Glentilt, Portsoy, and Kildrumie.

The ancients manufactured cloth out of the fibres of flexible asbestos, for the purpose, it is supposed, of wrapping up the bodies of the dead when exposed on the funeral pile. This cloth has also been made in modern times, the chief artifice seeming to consist in the admixture of flax and a liberal use of oil, both which substances are afterwards consumed by exposing the cloth for a certain time to a red heat. Gloves are made of it for holding red-hot crucibles, &c. The cloth of asbestos, when soiled, is restored to its primitive whiteness by heating in the fire. Ignition impairs the flexibility of asbestos in a slight degree.—U.

ASBOLAN. See COBALT, EARTHY.

ASBOLINE. A nitrogenous substance contained, according to Braconnot (Ann. Ch. Phys. [2] xxxi. 37), in soot (ἀσβολη). It is extracted by boiling the soot with water, evaporating, redissolving in water, adding hydrochloric acid to the solution, washing the pitchy precipitate with cold water, then boiling it with water, filtering after cooling, evaporating again, and treating with boiling water till no deposit forms on cooling. The liquid then yields by evaporation a kind of varnish, partially soluble in alcohol; and on treating the residue with ether and evaporating, asboline remains in the form of a yellow, very acrid, bitter, volatile oil, which is lighter than water, burns with flame, and yields an ammoniacal product by distillation. Asboline dissolves in nitric acid, yielding picric and oxalic acids. Its aqueous solution is coloured deep red by alkalis, forms an orange-coloured precipitate with acetate of lead, reduces nitrate of silver, and is precipitated by infusion of galls.

ASCLEPIADIN. A bitter emetic principle, contained in the *Asclepias vincetoxicum.* It is insoluble in water, alcohol, and alcoholic ether. It appears not to contain nitrogen. (Fenelle, J. Pharm. [2] xi. 565.)

ASCLEPIONE. $C^{20}H^{34}O^3$.—When the white milky juice of *Asclepias syriaca* is heated, the albumin contained in it coagulates, and on treating the coagulum with ether, and evaporating, asclepione is deposited in finely radiated or cauliflower-like groups of crystals. It is tasteless, inodorous, quite insoluble in water and alcohol, but dissolves readily in ether, less easily in oil of turpentine, naphtha, and strong acetic acid. It melts at 104° C., and then remains amorphous. At a higher temperature, it decomposes, giving off the odour of burnt caoutchouc. It is not attacked by strong boiling potash. (List, Ann. Ch. Pharm. lxix. 125.)

ASH OF ORGANIC BODIES. When any part of an organised body, vegetable or animal, is burnt with free access of air, part of it is resolved into volatile compounds, chiefly water, carbonic anhydride, and free nitrogen, while the other, and generally the smaller portion, is left as incombustible residue or **ash.** This residue may contain the following elements: —

Basic.	*Acid.*
Potassium	Chlorine
Sodium	Bromine
Calcium	Iodine
Barium	Phosphorus (as phosphoric acid)
Iron	Sulphur (chiefly as sulphuric acid)
Magnesium	Silicon (as silicic acid)
Manganese	Carbon (as carbonic acid, and occasionally as cyanogen).
Aluminium	
Copper	
Zinc	
(Lead, nickel, cobalt, tin)?	

These substances are the so-called inorganic or mineral constituents of the vegetable or animal structure; they are essential to its existence, and are associated with the organic matter in certain definite forms, not necessarily the same as those which they assume in the ash. It must be remembered, however, that the distinction between the organic and inorganic elements of an organised body is by no means absolute: for the carbon and oxygen, which are never absent from the ash, belong essentially to the organic structure of the body. Perhaps the best distinction between the organic and inorganic constituents of a plant or animal body is, that the former, viz. the carbon, hydrogen, oxygen, and nitrogen, are derived, in great part at least, from the air, whereas the latter are derived exclusively from the soil.

The inorganic constituents above enumerated are not all of equal importance to the existence of organised structures, or of equally frequent occurrence. Potassium, sodium, calcium, magnesium, and iron, associated with phosphoric acid, sulphuric acid, carbonic acid, silicic acid, and chlorine, are almost always present, in greater or lesser quantity, in the ashes of organised bodies, whether vegetable or animal; fluoride of calcium, in very small quantity, appears also to be an almost invariable constituent; and manganese, also in small quantity, is of frequent occurrence; the other elements are of rare or doubtful occurrence.

The mineral constituents of plants and animals vary greatly in amount, as well as in composition. In *bone*, the inorganic matter constitutes from ½ to ¾ of the entire mass, the amount in individual cases depending upon the age and species of the animal; in the higher classes of animals, the bone-ash consists mainly of phosphate of calcium, with a smaller quantity of carbonate; in the lower classes, the proportions of these constituents are reversed. Phosphate of calcium occurs also in the ashes of the *albuminous principles*, both of plants and animals, and is especially abundant in the *seeds* of cereal and leguminous plants; phosphate of magnesium is abundant in the ash of wheat-grain. The alkaline chlorides are very widely diffused throughout the bodies of plants and animals; chloride of sodium is invariably present in the fluids of the animal body and in the juices of plants. Alkaline carbonates are always present in the *blood*, and appear to be essential to the solution of the albuminous principles. Carbonate of potassium forms the greater part of *wood-ash*. **Silica** is scarcely ever absent from the ashes of organised bodies. The ashes of *equisetaceous plants* contain 97 per cent. of silica. The hard external sheathing of the stems of *grasses* consists of silicate of potassium. The shields of the lowest classes of animals, *infusoria*, &c., consist mainly of silica, which is so thickly deposited in their organs, that neither decomposition nor incineration can destroy their form: hence it is that deposits of infusoria are so often discovered. In the tissues and juices of the higher classes of animals, silica occurs only as an incidental constituent, though it is seldom altogether absent. According to Gorup-Besanez (Ann. Ch. Pharm. lxvi. 342), it forms an integral constituent of *feathers* and of *hair*.

Sulphur occurs to the amount of about 1 per cent. in all the albuminoïdal substances, and is converted during incineration into sulphuric acid, which is found in the ash as alkaline sulphate, sometimes however more or less reduced to sulphide by the action of the carbon at a high temperature. The juices of the animal body and of plants also contain small quantities of alkaline sulphates and sulphate of calcium.

Iron is always present in vegetable and animal tissues and fluids, and is found in the ash as sesquioxide, either free or as basic phosphate.

Alumina has been found in considerable quantity in the juice of plants which exhibit an acid reaction, *e. g.* in *Lycopodium chamæcyparissus*, *L. clavatum*, and *L. denticulatum* (Salm-Horstmar, J. pr. Chem. xl. 302; Aderholdt, Ann. Ch. Pharm. lxxxii. 111; Solms-Laubach, *ibid.* c. 297). In most other plants, alumina is altogether absent, any small quantities that may be found in the ash, generally arising from impurity in the reagents, especially in the caustic potash or soda, or from want of due care in cleansing the leaves, roots, or other parts under examination, from adhering particles of soil.

The other metals above-mentioned as occasional constituents of ashes, occur only in very small quantity, their presence being mostly, perhaps, due to some peculiarity in the nutrition of the plant or animal in which they are found. A peculiar kind of violet (*Viola calaminaris*) with yellow flowers, was found by A. Braun (Pogg. Ann. xcii. 175) to contain **zinc**, which metal was likewise found in the soil, its presence doubtless determining the production of the peculiar variety of the plant. The ash of the blue blood of *Limulus cyclops* was found by Genth (Pogg. Ann. xcv. 60) to contain 0·08 to 0·33 per cent. of **oxide of copper**. The occurrence of **titanic acid** in plant-ashes is mentioned by Städeler (Wöhler's prakt. Chem. Uebungen, 1853 p. 173), of **baryta** by Scheele (in 1788), and more recently by Eckard (Ann. Ch. Pharm. c. 294), and by Forchhammer (Pogg. Ann. xcv. 60; Jahresber d. Chem. 1859, p. 987). On the occurrence of copper and other metals in plant-ashes, see also Jahresber. 1847—8, p. 874; 1849, p. 430; 1852, p. 702; 1853, p. 604.

As the mineral constituents of plants are all derived from the soil and vary greatly both in amount and in composition, it will be easily understood that the examination of plant-ashes is of great importance with reference to agriculture. A plant will not grow on soil deficient in the mineral substances which it requires; if phosphoric acid is deficient, wheat and other cereal grasses cannot form their seed in its normal amount; if there is a deficiency of silica, the straw will be weak. Some plants require abundance of alkali, others of lime, &c. The examination of the ash shows what particular mineral substances the plant requires, and consequently what substances must be supplied to it artificially in the form of manure, if they are not already contained in the soil.

We now proceed to describe the preparation and analysis of ashes.

Preparation of the Ash.—The substance to be incinerated must in the first place be carefully freed from extraneous matter. Herbs, roots, and barks, which are especially liable to be contaminated with adhering mould, clay, or sand, must first be cleaned from the grosser impurities by scraping, or otherwise, and then washed with a slightly moistened sponge to remove the fine dust; washing with large quantities of water is objectionable, as it may remove some of the soluble salts. Seeds are best cleaned by pouring distilled water upon them in a glass jar, stirring for a little while with a rod, and then pouring the whole on a coarse sieve, which allows the fine dust to run through, but retains the seeds. After repeating this treatment two or three times, the seeds may be further cleansed by rubbing them between a linen cloth. Animal substances are less liable to contamination with mechanical impurities: their incineration is often facilitated by exhausting them with water, and incinerating separately the aqueous extract and the residue. The quantity of material incinerated should be such as to yield from 4 to 6 grammes of ash. Of seeds, roots, barks, and leaves, which are for the most part rich in mineral constituents, from 100 to 200 grammes of the dried substance is generally sufficient; of wood, two or three times that quantity must be taken; of animal substances containing a large amount of water, it is often necessary to incinerate a much larger quantity. The substance should, previous to incineration, be carefully dried and somewhat comminuted; seeds, however, if not very large, are best incinerated without comminution.

The incineration must be conducted with great care, as the constitution of the ash is often materially affected by the manner in which it is performed. The chlorides of potassium and sodium, though fixed at comparatively low degrees of heat, volatilise perceptibly at the high temperature sometimes attained during the incineration, especially in a current of air; this is still further the case with iodides. Moreover, by the joint action of silica and charcoal, phosphates may be decomposed and phosphorus volatilised; sulphates also reduced to sulphides, or sulphuric acid driven off. And even when no actual loss takes place, different modes of incineration may give rise to considerable differences in the composition of the ash. Carbonates in an ash generally result from the combustion of salts of organic acids existing in the substance burned; they may, however, be introduced in other ways. If tribasic phosphate of sodium be ignited in presence of a large quantity of organic matter, sugar, for example, till the organic matter is charred, and the mass be then lixiviated with water, a solution of carbonate of sodium is obtained, and the residue, after the charcoal has been completely burned away, consists of pyrophosphate of sodium, the carbonic acid produced by the combustion of the organic matter having decomposed the tribasic phosphate, taken away 1 at. of the base, and converted it into carbonate. If, on the other hand, the mass be at once completely incinerated without lixiviation of the charcoal, nothing but tribasic phosphate will be obtained. In all cases then, in which the arrangement of the mineral constituents of an organised structure is to be inferred from the composition of the ash, great care must be taken to guard against or allow for any such modifications as that just noticed. In the examination of plant-ashes for agricultural purposes, such questions are indeed of minor importance, the chief object of the investigation being to determine the ultimate constituents of the ash; but in physiological inquiries, the actual arrangement of the mineral constituents in the living structure is often a point of great importance.

The difficulty of incinerating an organic substance is greatly increased when the ash is easily fusible, the decompositions just considered being then most likely to occur. Leaves, herbaceous stems, roots, bark, &c., which chiefly contain infusible salts of the alkaline earths, are comparatively easy to burn; but seeds, and many animal substances, such as dried blood, which contain large quantities of alkaline salts, are very troublesome, and require great care in regulating the temperature.

The method of incineration originally practised, especially for the preparation of plant-ashes, consisted in burning the dried substance in a Cornish or Hessian crucible, laid obliquely in the fire, and kept at a moderate red heat. The carbon then burns away with greater facility, the looser the texture of the charred mass, and the less its position and form are altered by movement and stirring. The objections to this method are that it often gives incorrect results regarding the amount of phosphoric acid, carbonic acid, and chlorine, inasmuch as chlorides are decomposed by the action of acid phosphates in presence of water, and at very high temperatures, phosphorus may be volatilised by the action of charcoal on acid phosphates. Extraneous matters may also be introduced into the ash by the action of phosphates in a state of fusion on the crucible.

A much better method is that recommended by **Erdmann**, which consists in incinerating the plant or animal substance in a muffle built into the mouth of a furnace in such a manner that the heat may play upon it chiefly from the top. The incineration goes on most favourably at a distance of 3 or 4 inches from the front aperture of the muffle, and at a low red heat not visible by daylight. At this temperature, there is no danger either of the volatilisation of chlorides or of the fusion of phosphates. If the muffle be kept loosely closed by a clay stopper, sufficient air will enter to produce, in the course of twelve hours, a quantity of ash free from charcoal sufficient for an analysis. A convenient mode of proceeding is first to char the substance in a platinum or porcelain dish, and then heat the charred residue in the muffle in the manner just described; the charcoal then burns away with slight incandescence. The ash may afterwards be weighed in the dish.

Messrs. **Lawes** and **Gilbert** use cast-iron muffles 18 inches long, 3½ inches high, and 5 inches wide at the bottom. The muffle, which has a flange at the fore part, fits exactly into an orifice in a cast-iron furnace front; and a 1½ inch pipe proceeding from the farther end of the muffle, passes through the cast-iron furnace back, and serves to carry away the evolved gases. The muffle rests on a brick in the furnace, to lessen bottom heat and thus prevent fusion, the fuel being heaped up at the sides and top, chiefly the latter. The substance is burnt in large platinum sheets or dishes, the latter 10 inches long, 4 to 5 inches wide, and 1½ inch deep. By this arrangement, the access of ash from the fire is entirely avoided; the ash is burnt by surface, not by bottom heat; the draught of air is free; and the incineration may be accomplished at a very low temperature.*

This is by far the best mode of incineration yet devised; nevertheless it is occasionally attended with slight loss of sulphur, phosphorus, chlorine, iodine, &c. To obviate these losses, it has been proposed to mix the substance to be incinerated with lime, baryta, or other strong bases capable of retaining the acids. Wackenroder adds for this purpose, acetate or carbonate of calcium, or quick lime; Strecker proposes to moisten the dried and charred substance with such a quantity of baryta-water, that the ash, after incineration, may contain about half its weight of baryta. The moistened charcoal is then dried and burnt in the muffle at as low a temperature as possible. To substances which produce ashes containing much carbonic and silicic acids, Way and Ogston, add for the same purpose, nitrate of barium; Slater adds peroxide of barium; Verdeil, nitrate of ammonium; and Will, mercuric oxide; but all these admixtures are attended with peculiar inconveniences, which stand in the way of their general application.

H. Rose adds a weighed quantity of carbonate of sodium, chars the substance in a crucible, and burns away the charcoal by directing a stream of oxygen upon it through an aperture in the lid. This method effects a complete and rapid combustion of the charcoal, but the high temperature produced often causes the ash to fuse, and then the crucible is attacked. Crucibles of stone-ware (*Steingut*) withstand the action better than those of porcelain.

[For the methods of Mitscherlich and Hlasiwetz, see Handw. d. Chem. 2te Aufl. ii. 352; for the latter also, Ann. Ch. Pharm. xcvii. 244.]

Analysis of the Ash.—Of the various methods which have been given for the analysis of ashes, the simplest and most generally applicable is that of Professor Will (Handw. d. Chem. 2te Aufl. ii. 361; Conington's Handbook of Chemical Analysis, p. 226). The ash prepared in the muffle at the lowest possible temperature, is triturated to a uniform powder, and preserved in a stoppered bottle. One portion of it is used to determine the carbonic acid by one of the methods given under ALKALIMETRY, p. 119. A second is treated with dilute nitric acid, and the filtrate is used for determining the chlorine by precipitation with nitrate of silver; while a third portion (4 or 5 grammes) is used for determining the silica and the other constituents. For this last purpose, the ash is treated with hydrochloric acid; the silica separated by complete evaporation to dryness, and digestion of the residue with water containing hydrochloric acid (see SILICA); and the quantity of the filtrate, together with the washings, is determined, either by weight or by measure.

In one portion of this filtrate, of known weight or volume, the sulphuric acid is determined by precipitation with chloride of barium; in a second, the lime, magnesia, sesquioxide of iron (alumina, if present), and the phosphoric acid; in a third, the alkalis.

Lime, Magnesia, Ferric Oxide, Phosphoric Acid.—If, as in the ashes of seeds and of many animal substances, all the bases, or the greater part of them, are present as phosphates, the liquid is first supersaturated with ammonia (or mixed with acetate of sodium), then with acetic acid, and the undissolved ferric phosphate, $Fe^4O^6.cP^2O^5$, is collected and weighed (together with phosphate of aluminium, if present, which may afterwards be separated by potash). The lime is next precipitated by oxalic acid, then part of the phosphoric acid and all the magnesia by ammonia, and the rest of the phosphoric acid by a magnesium-salt. In ashes containing a smaller proportion of phosphoric acid, part or the whole of the magnesia remains in solution after this treatment. This portion is determined by precipitation with phosphate of sodium, or (if the filtrate is to be afterwards used for the determination of the alkalis) with phosphate of ammonium. If manganese is likewise present (as a manganous salt), the ferric phosphate is first precipitated as above; the liquid filtered from the precipitate is mixed with a known volume of a standard solution of ferric chloride made as neutral as possible; the whole is heated to boiling; the precipitate thoroughly washed with hot water and dried; and from its weight, that of the (anhydrous) phosphoric acid is found by deducting the weight of the ferric oxide added†; to this quantity of phosphoric acid, must be added that which was previously determined as ferric phosphate (and phosphate of aluminum). In the filtrate, which contains manganese, calcium, and magnesium, these metals are determined by the usual methods, the manganese being precipitated as peroxide by hypochlorite of sodium, the precipitate collected after twenty-four hours, then ignited or weighed as manganoso-manganic oxide (Mn^3O^4).

Alkalis.—The ash, dissolved in hydrochloric acid, not in great excess, is mixed with

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* For the above description, the Editor is indebted to the kindness of Dr. Gilbert.

† The amount of phosphoric acid in this precipitate might be determined directly by dissolving in hydrochloric acid, adding sufficient tartaric acid to prevent precipitation of iron and alumina by alkalis, then adding excess of ammonia, and precipitating by a magnesium-salt.

oxalic acid, then with excess of ammonia, and if magnesia is still in solution with phosphate of ammonium.* The precipitate is washed with ammoniacal water; the filtrate is evaporated a little to expel the excess of ammonia, and mixed while still hot with acetate of lead; the liquid is again filtered, and the excess of lead removed by ammonia and carbonate of ammonium; the filtrate from this precipitate, together with wash-water, is evaporated, with addition of sal-ammoniac; and the ammoniacal salts are expelled by gentle ignition. The residue, which contains nothing but the chlorides of potassium and sodium, is then weighed, and the relative quantities of the two chlorides are determined, either by precipitating the potassium with dichloride of platinum, or determining the amount of chlorine by precipitation with nitrate of silver. (See ANALYSIS, INDIRECT, p. 220.)

Knop and Arendt (Chem. Centralbl. 1857, 169), determine the phosphoric acid in ashes by adding *uranic acetate* to the solution, acidulated with acetic acid as above, whereby a precipitate of ammonio-uranic phosphate is produced, which, when ignited with addition of a few drops of nitric acid, leaves uranic phosphate, containing $2Ur^4O^3.P^2O^5$. (For the details of the method, see PHOSPHORIC ACID, under PHOSPHORUS.)

For other methods of ash-analysis, see Fresenius and Will, Ann. Ch. Pharm. l. 363; Erdmann, J. pr. Chem. xxxviii. 20; H. Rose, Pogg. Ann. lxxx. 94, and Handb. d. Analyt. Chem. ii. 766; Mitscherlich, J. pr. Chem. xxxv. 231; Wackenroder, Arch. Pharm. [2] liii. 1; Städeler, Prakt. Uebungen in der Chem. Anal. von Wöhler, 1853, 172; Wittstein, Pharm. Centralbl. 1853, 761. Also for a description of all these methods, Handw. d. Chem. 2te Aufl. ii. 353.

For the composition of the ash of individual plants, see the names of the plants in this dictionary. Extensive tables of the composition of plant-ashes are given in the first five volumes of Liebig and Kopp's *Jahresbericht für Chemie*, 1847 to 1852. The new edition of Ure's *Dictionary of Arts, Manufactures, and Mines* (i. 212), also contains a table showing the average composition of the ash of some of the most useful agricultural plants.

ASH, VOLCANIC. This name is applied to the pulverulent portion of the matter thrown out by volcanos. The ash emitted by different volcanos, by the same volcano at different times, and even at different stages of the same eruption, exhibits great differences of structure and composition. It is sometimes dark-coloured or even black, and composed of earthy or soft particles, sometimes grey or white, and finely divided. In the eruption of Vesuvius, A.D. 79, which overwhelmed Pompeii and Herculaneum, the ash was so fine and dry that it took exact casts of objects buried in it. It is this finely divided matter to which the term ash is especially applied, the coarser varieties being generally denominated volcanic sand; it sometimes rises to considerable heights, and is then carried by the wind to great distances. In the eruption of Coseguina, on the Bay of Conchagua, in Guatemala (1835), some of the ash fell at Kingston in Jamaica, at a distance of 700 miles.

Volcanic ash, when examined by the microscope, appears to be composed of fragments of lava, slag, mica, felspar, magnetic iron ore, augite, pumice, olivine, &c. It is therefore a mechanical mixture of minerals and rocks abraded by trituration against each other. In the ash thrown out by Vesuvius on the 22nd of October 1822, Vauquelin found 28 pts. silica, 8·0 alumina, 18 gypsum, 20·88 iron pyrites, 2·6 lime, and 1 carbon, together with 41·42 pts. sulphate of copper, sulphate of ammonium, chlorides, and sulphur. In the ash emitted from the crater of the Soufrière in Guadaloupe, in 1797, Dufrénoy (Ann. Ch. Phys. [2] lxvii. 251) found 2 per cent. of alum, potash, and gypsum, 8·84 water, 32·61 pts. of matter attacked by acids (which he regarded as labrador), and 56·23 pts. not attacked by acids (regarded as glassy felspar). In the ash thrown out by the same crater in the year 1836, Dufrénoy found 50·88 pts. of matter insoluble in acids, 33·72 pts. soluble in acids, 6·93 water and 0·62 sulphur (loss 1·85 per cent.)

The following table contains the results of a few more recent analyses: *a*, *b*, ash from the above-mentioned eruption of Coseguina (Dufrénoy and Élie de Beaumont, Ann. Ch. Phys. [2] lxviii. 266); this ash contained 18 pts. of matter decomposible by hydrochloric acid (*a*), and 82 pts. unattacked by that acid (*b*). *c*, Ash from Gunnung-Gurtur, in Java; eruption of January 4th, 1843 (Mayer, Leonhard and Bronn's Jahrb. d. Miner. 1853, 463). *d*, Ash from the same volcano; eruption of November 25th, 1843. Of this ash, water dissolved 0·3 per cent. consisting of lime and magnesia-salts (Schweitzer, J. pr. Chem. lxv. 194). *e*. So-called *ferric* ashes, and *f*, so-called *ferrous* ashes from Etna (Sartorius von Waltershausen, "Vulcanishe Gesteine," Göttingen, 1853, 172). *g*. Ash from the eruption of Hecla in 1846 (Genth, *ibid.* 176).

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* For other methods of separating magnesia from the alkalis, see MAGNESIUM.

	a	b	c	d	e	f	g
Silica	51·7	64·3	34·2	51·6	48·7	51·3	56·9
Alumina . . .	15·2	21·1	37·5	21·9	17·9	18·4	14·2
Ferric oxide . . .	13·0	—	18·2	—	12·7	—	—
Ferrous oxide . .	—	—	6·7	10·8	—	11·7	13·9
Lime	11·1	1·4	0·7	9·3	5·5	7·5	6·2
Magnesia . . .	—	0·7	—	3·3	2·5	4·3	4·0
Soda	6·2	9·6	—	2·9	4·5	4·6	2·3
Potash	—	—	—	0·5	2·0	1·6	2·6
Water and loss . .	2·8	3·4	1·0	0·6	6·6	0·5	—
Matter soluble in water	—	—	1·7	0·3	—	2·7	—
	100·0	100·5	100·0	101·2	101·4	102·6	100·1

ASPARAGINE. $C^4H^8N^2O^3$, or $C^8H^8N^2O^6$. *Altheine, Asparamide.* (Gm. x. 239.)—This substance was discovered in 1805 by Vauquelin and Robiquet (Ann. Chim. lvii. 88). It exists ready formed in many plants, viz. in common asparagus (*Asparagus officinalis*), in the marsh-mallow (*Althaea off.*), in comfrey (*Symphytum off.*), in potatoes, in chestnuts, in the leaves of the deadly nightshade (*Atropa Belladonna*), in liquorice-root, in the root of *Robinia pseudacacia*, in *Convallaria majalis*, and *C. multiflora*, in the milky juice of the lettuce, in the tubers of the dahlia, and in the young shoots of vetches, peas, beans, and several other leguminous plants grown in the dark. According to Piria (Ann. Ch. Phys. [3] xxii. 160), the young shoots of these plants, when formed in the light, contain just as much asparagine as when they are grown in the dark; but the asparagine disappears as the plant arrives at the flowering stage. On the other hand, Dessaignes and Chautard (J. Pharm. [3] xiii. 245), and likewise Pasteur (Ann. Ch. Phys. [3], lxxxi. 70), find that vetches growing in light are free from asparagine.

Preparation.—The juice obtained from the young shoots of *asparagus*, filtered and evaporated to a syrup, deposits after standing for some days, crystals of asparagine, which may be purified by recrystallisation from water. As the mucus of the plant impedes the crystallisation, it is best to leave the shoots to ferment for a few days in a warm place, and then bruise and press them, with addition of water; by this treatment the mucus is decomposed. In a similar manner, asparagine may be obtained from marsh-mallow roots, and from the young shoots of vetches, &c. grown in the dark. To obtain asparagine from liquorice-root, the root is cut into pieces and exhausted with water; the liquid boiled to precipitate the albumin, then mixed with acetic acid to separate the glycyrrhizin contained in the root, and afterwards with acetate of lead, which throws down phosphate and malate of lead, together with brown colouring matter; and the excess of lead is removed by sulphydric acid. The filtered liquid evaporated to a small bulk, deposits crystals of asparagine after a few days.

Asparagine forms hard brittle crystals, $C^4H^8N^2O^3.H^2O$, belonging to the trimetric system. The ordinary form is a right rhombic prism, $\infty P\ .\ oP\ .\ m\breve{P}\infty\ .\ \infty\bar{P}\infty$, with the hemihedral faces $\frac{P}{2}$. Inclination of the faces, $\infty P : \infty P = 129° 37'$; $\frac{P}{2} : oP = 116°\text{-}57'$; $m\breve{P}\infty : oP = 120° 46'$. Specific gravity 1·519 at 14° C. The crystals are inodorous, have but a slight taste, and are permanent in the air. They give off water of crystallisation at 100° C. They dissolve in 11 pts. of cold, and 4·44 pts. of boiling water; the solution has a slight acid reaction. Asparagine dissolves also in acids and in alkalis. It is insoluble in cold absolute alcohol, and nearly insoluble in that liquid at higher temperatures; insoluble also in ether and in oils, whether fat or volatile.

Asparagine dissolved in water and in alkalis, deflects the plane of polarisation of a ray of light to the left; but when dissolved in acids, it deflects the plane of polarisation to the right. The specific rotatory power of an acid solution is + 35°, and of an ammoniacal solution, − 11° 18'..

Asparagine heated with strong acids or alkalis, is resolved into aspartic acid and ammonia:

$$C^4H^8N^2O^3 + H^2O = C^4H^7NO^4 + NH^3.$$

The crystals subjected to dry distillation also give off ammonia, and leave aspartic acid. Asparagine dissolved in cold nitric acid, yields aspartic acid and nitrate of ammonium, but when subjected to the action of nitrous acid, as when nitric oxide gas is passed through a solution of asparagine in pure and moderately strong nitric acid, it is converted into malic acid, with evolution of nitrogen:

$$C^4H^8N^2O^3 + N^2O^3 = C^4H^6O^5 + N^4 + H^2O$$

The solution of pure asparagine-crystals may be kept unaltered; but if the crystals are coloured, their solution soon passes into a state of fermentation, and the whole of the asparagine is converted into succinate of ammonium:

$$C^4H^8N^2O^3 + H^2O + H^2 = C^4H^4(NH^4)^2O^4.$$

The hydrogen is derived from the fermenting matter. A solution of perfectly pure asparagine experiences the same change when mixed with a small quantity of the juice expressed from the young shoots of vetches (Piria). Asparagine ferments also under the influence of casein, and is converted first into aspartate of ammonium, afterwards into succinate.

Asparagine forms definite compounds with acids. The *hydrochlorate*, $C^4H^8N^2O^3.HCl$, is obtained in large crystals either by dissolving 1 at. asparagine in 1 at. hydrochloric acid, evaporating at a gentle heat, and adding alcohol; or by passing dry hydrochloric acid gas over finely pounded crystals of asparagine, exposing the resulting compound to the air till it no longer gives off acid vapours, then dissolving in hot water, and leaving the solution to cool.

Asparagine also forms salts in which 1 at. of its hydrogen is replaced by a metal; thus the *copper-salt* is $C^4H^7CuN^2O^3$. These salts are obtained by mixing a solution of asparagine with the corresponding oxides. Asparagine also unites with chloride of mercury and nitrate of silver.

Asparagine has the same composition as malamide, $N^2(H^4.C^4\overset{''}{H}{}^4O^3)$, and its conversion into malic acid by the action of nitrous acid, suggests the idea that it may be really the amide of that acid. According to Demondesir, however (Compt. rend. xxxiii. 227), and Pasteur (Ann. Ch. Phys. [3] xxxviii. 437) the amide obtained by the action of ammonia on malic ether, differs from asparagine in crystalline form and in other properties.

ASPARAGOLITE. An old name of the variety of apatite which has the green colour of asparagus.

ASPARAGUS OFFICINALIS. The ashes of wild and cultivated asparagus, and of the young heads of the cultivated plant, have been analysed by T. J. Herapath (Chem. Soc. Qu. J. ii. 9). 100 parts of the fresh wild plant yielded 2·42 pts. of ash; 100 pts. of same dried, 6·07 per cent. ash. The cultivated plant yielded in the fresh state 1·53, and in the dry state 6·07 per cent. ash. The young heads in a state fit for the table gave 0·81 per cent. and 11·24 per cent. ash. The constituents of the several ashes are as follows:—

Soluble in water:		Wild.	Cultivated.	Young Heads.
Anhydrous	Carbonic acid	4·86	14·27	4·01
	Sulphuric acid	7·77	3·56	31·08
	Phosphoric acid	trace	2·10	
	Potash	15·81	32·74	32·63
	Soda	2·72	—	
	Chloride of sodium	20·51	trace	10·06
	Chloride of potassium	—	13·06	
Insoluble:				
	Carbonate of calcium	21·43	14·61	6·96
	Carbonate of magnesium	2·62	—	—
	Basic *c*-phosphate of calcium	21·67	16·21	14·05
	Basic ferric *c*-phosphate	1·70	0·46	0·21
	Silica	0·85	2·97	1·00
	Sulphate of calcium	trace	trace	trace
	Basic phosphate of magnesium	trace	trace	trace
		99·94	99·98	100·00
	Soluble in water (per cent.)	51·67	57·64	7·78
	Insoluble " "	48·27	42·34	22·22

ASPARAMIDE. Syn. with ASPARAGINE.

ASPARAMIC ACID. Syn. with ASPARTIC ACID.

ASPARTIC ACID. $C^4H^7NO^4$, or $C^8H^7NO^8$. (Plisson, Ann. Ch. Phys. xxxv. 175, xl. 303.—Plisson and O. Henry, *ibid.* xlv. 315.—Boutron-Chautard and Pelouze, *ibid.* lii. 90.—Liebig, Pogg. xxxi. 232, Ann. Ch. Pharm. xxvi. 125, 161.—Piria, Ann. Ch. Phys. [3] xxii. 160.—Dessaignes, Compt. rend. xxx. 329; xxxi. 342; Ann. Ch. Pharm. lxxxiii. 83.—Pasteur, Ann. Ch. Phys. [3] xxxiv. 30; Ann. Ch.

Pharm. lxxxii. 324.—Gm. x. 230; Gerh. i. 812.)—This acid, which is isomeric, if not identical with malamic acid, $O\left\{\begin{matrix}N.(H^2.C^4H^4O^3)\\H\end{matrix}\right.$, is obtained either by the decomposition of asparagine, chiefly under the influence of acids or alkalis, or by the action of heat on the acid malate, maleate, or fumarate of ammonium. The acids obtained by these two processes are identical in composition, but differ in their relations to polarised light, the former being optically active, the latter inactive.

To prepare *active aspartic acid*, asparagine is boiled: 1. With water and oxide of lead, as long as ammonia continues to escape, the water being replaced as it evaporates: the resulting aspartate of lead, after being purified by boiling with water and alcohol, is decomposed by sulphydric acid, and the filtered solution is evaporated till it crystallises (Plisson).—2. With baryta-water, the aspartate of barium being decomposed by sulphuric acid (Boutron and Pelouze).—3. With potash, the liquid being afterwards evaporated to dryness with excess of hydrochloric acid, and the chloride of potassium dissolved out by water, which leaves the aspartic acid undissolved and perfectly free from potash (Liebig).—4. With hydrochloric acid, for three hours, the solution being then evaporated to dryness, and the residual chloride of ammonium and hydochlorate of aspartic acid dissolved in a small quantity of water and half neutralised with ammonia; the liquid on cooling deposits a considerable quantity of aspartic acid. (Dessaignes.)

Active aspartic acid crystallises in very small thin, shining, rectangular plates, truncated at the angles; they belong to the trimetric system. Specific gravity 1·6613 at 12·5° C. It is much less soluble in water than asparagine, 1 pt. of it requiring 364 pts. of cold water to dissolve it. In boiling water it dissolves more readily, but is nearly insoluble in alcohol. It dissolves readily in alkalis, and the solutions turn the plane of polarisation of a luminous ray to the left. It is also easily soluble in the stronger acids, and the solutions thus formed turn the plane of polarisation to the right. The specific rotatory power of the solution in hydrochloric acid is + 27° 86′. (Pasteur.)

Inactive Aspartic Acid is obtained by heating acid malate of ammonium to 200° C.; boiling the residue for some hours with hydrochloric acid; dissolving the hydrochlorate of aspartic acid, which crystallises from the liquid on cooling, in hot water, and half saturating the solution with ammonia. Inactive aspartic acid then separates in small crystals, belonging to the monoclinic system. Ordinary combination $\infty P . oP . [P\infty]$. Inclination of the faces, $\infty P : \infty P$ in the plane of the oblique diagonal and the principal axis = 128° 28′; $oP : \infty P = 91° 30′$; $[P\infty] : oP = 131° 25′$. The crystals are grouped in stars, and sometimes take a lenticular form. Specific gravity 1·6632 at 12′ 5° C. The inactive acid is more soluble in water than the active acid, 1 part of it dissolving in 208 pts. of water at 13·5° C. It dissolves very easily in hydrochloric and in nitric acid. The solutions have no action on polarised light. (Dessaignes, Pasteur.)

Aspartic acid is decomposed by heat, giving off ammonia and a faint empyreumatic odour, like that evolved in the destructive distillation of animal substances. It is not acted upon by boiling with hydrochloric acid or with dilute sulphuric acid, but when heated with strong sulphuric acid, it decomposes, and sulphurous acid is given off. It is not decomposed by pure nitric acid, but if nitrous acid is also present, as when nitric oxide gas is passed through a solution of aspartic acid or nitric acid, the aspartic acid is converted into malic acid, with evolution of nitrogen gas:

$$\underbrace{2C^4H^7NO^4}_{\substack{\text{Aspartic}\\\text{acid.}}} + N^2O^3 = \underbrace{2C^4H^6O^5}_{\substack{\text{Malic}\\\text{acid.}}} + N^4 + H^2O$$

Compounds of Aspartic Acid with Acids.—Both the active and inactive varieties of aspartic acid dissolve in the stronger acids, forming definite compounds, which by evaporation over the water-bath, or better by spontaneous evaporation, are obtained in crystals. The compounds are active or inactive to polarised light, according as they are obtained from the active or inactive acid.

The *active hydrochlorate*, $C^4N^7NO^4.ClH$, forms crystals belonging to the trimetric system; they are prisms with angles of about 90°, very much truncated on two opposite lateral edges, and terminated by faces inclined at an angle of about 115°, and belonging to an irregular tetrahedron. The crystals deliquesce in the air, the aspartic acid being set free. They are decomposed by solution in water, but the addition of a few drops of hydrochloric acid prevents the decomposition. Specific rotatory power of the solution + 24·4°. The crystals are decomposed by heat, giving off water and hydrochloric acid, and leaving fumarimide. The crystals of the *inactive hydrochlorate* belong to the monoclinic system, and differ altogether in appearance from those of the active compound. Ordinary combination ∞P . ∞P∞ . −P . oP . +mP∞. Inclination of the faces oP : ∞P∞ = 119° 45′; ∞P∞ : ∞P = 123°. The crystals are nearly unalterable in the air, only in summer losing their lustre and transparency, and becoming milk-white on the surface. They decompose when dissolved in water, but the inactive acid being more soluble than the active acid, is not precipitated; if, however, alcohol be added, an abundant precipitation takes place. The inactive hydrochlorate is decomposed by heat like the active salt.

The *sulphate*, $C^4H^7NO^4.SO^4H^2$, is obtained by gradually adding aspartic acid to strong sulphuric acid heated to 50° or 60° C. in a wide glass tube, and leaving the tube closed for a few days; it then separates in large agglomerated prisms, which are lighter than the mother-liquor (Dessaignes). The *nitrate* is obtained, like the hydrochlorate, in beautiful crystals.

Aspartates.—Aspartic acid is monobasic, the formula of its normal salts being $C^4H^6MNO^4$. It likewise forms basic salts, the composition of which is not very clearly made out. The aspartates of the alkali-metals are soluble, and taste like broth. The active and inactive aspartates agree in composition, and in most of their properties, differing only in solubility, crystalline form, and relation to polarised light.

The *ammonium* and *potassium* salts are very soluble and difficult to crystallise.

The *sodium-salts*, $C^4H^7NaNO^4.H^2O$, are obtained by neutralising the acid with caustic soda or its carbonate, and leaving the solutions to evaporate slowly; they are perfectly neutral. The *active salt* crystallises in prismatic needles belonging to the right prismatic system, and terminated by faces of a tetrahedron inclined to one another at about 106°. The four faces of this tetrahedron are either present alone, or are much more developed than those of the opposite tetrahedron, which, if equally developed with the former, would constitute a rhombic pyramid; 1 part of this salt dissolves in 1·12 pts. of water at 12·2 C. The specific rotatory power of the solution is −2° 23′. The salt gives off its water of crystallisation at 160° C., turns yellow and gives off ammonia at 170°, and froths up considerably at higher temperatures. The *inactive sodium-salt* crystallises in the monoclinic system, the ordinary combination being ∞P . ∞P∞ . oP . +P. Inclination of the faces, oP : ∞P∞ = 144° 46′; ∞P : ∞P, in the plane and of the oblique diagonal and principal axis = 51° 38′; +P : +P = 112° 53′. The salt often forms twin-crystals, with the face of junction ∞P∞. One pt. of the salt dissolves in 1·19 pts. of water at 12·5° C.

Normal barium-salt, $C^4H^6BaNO^4.2H^2O$.—The active salt crystallises in very slender silky needles soluble in water, and giving off 14·4 per cent. water at 120° C. (Dessaignes). The *inactive normal salt* forms an uncrystallisable gummy mass (Wolff). The *basic* barium-salt is obtained by gradually adding hydrate of barium to a hot and rather strong solution of the normal salt. The liquid solidifies on cooling in a crystalline mass, but by recrystallisation from boiling water in a vessel protected from the carbonic acid of the air, this salt may be obtained in rather large shining prisms containing $2C^4H^6BaNO^4.Ba^2O + 5H^2O$. In vacuo, the crystals give off 3 at. water; when heated to 160° C. they lose 16·4 per cent., and the residual salt contains, according to Dessaignes, 57·05 per cent. Ba^2O, agreeing nearly with the formula $C^4H^5Ba^2NO^4$, which requires 57·55 per cent. This is the formula of the normal salt of a dibasic acid; but since aspartic acid is in all probability an amidogen-acid, and such acids are always monobasic, it is rather to be supposed that the true formula of the salt dried at 160° C. is $2C^4H^6BaNO^4.Ba^2O$. This formula requires only 55·0 per cent. Ba^2O; the greater proportion obtained by Dessaignes may have been due to the presence of carbonate of barium. (Gerhardt, Traité, i. 818.)

The *normal calcium-salt* is gummy, and tastes like the sodium-salt. The *basic* salt frequently forms prismatic crystals containing $2C^4H^6CaNO^4.Ca^2O + 7H^2O$; according to Dessaignes, it gives off 8 atoms of water at 160° C., and is then reduced to $C^4H^5Ca^2NO^4$.

Magnesium-salts.—The normal salt forms crystalline crusts, soluble in about 16 pts. of boiling water, insoluble in absolute alcohol. The basic salt obtained by dissolving magnesia in the normal salt is a gummy mass.

Aspartate of Zinc is a white non-deliquescent salt. *Aspartate of nickel* is obtained by evaporation in a green fissured mass. An aspartate of *iron* is precipitated on adding a solution of basic aspartate of magnesium to sesquichloride of iron.

Aspartates of Copper.—The normal salt of the active acid exists only in solution. A basic salt is obtained by adding a solution of the normal barium-salt to a hot solution of sulphate of copper. The liquid on cooling deposits pale blue, very light crystals which, according to Dessaignes, contain $C^4H^5Cu^2NO^4.5H^2O$ (or rather, perhaps, $2C^4H^6CuNO^4.Cu^2O + 9H^2O$), and give off their water at 160° C., leaving the anhydrous salt $C^4H^5Cu^2NO^4$. Inactive aspartate of ammonium forms a bluish precipitate with copper-salts. (Wolff.)

Aspartates of Lead.—The normal lead-salt, $C^4H^6PbNO^4$, is obtained by precipitating a solution of acetate of lead with aspartate of potassium or basic aspartate of calcium. On mixing an ammoniacal solution of normal acetate of lead with inactive aspartate of sodium, a curdy precipitate is formed, and the filtered liquid, if diluted with a considerable quantity of water, deposits, after two or three days, nacreous crystals united in very hard spherical masses. These crystals are anhydrous, and contain 63·88 per cent. of lead-oxide, agreeing with the formula $2C^4H^6PbNO^4.Pb^2O$, which requires 64·5 per cent. Pb^2O. The formula $C^4H^5Pb^2O^4$, analogous to that of the basic aspartates examined by Dessaignes, would require 66·1 per cent. of lead-oxide (Pasteur). The sodium-salt of active aspartic acid also forms a precipitate with ammoniacal acetate of lead, and the liquid afterwards deposits hard radiated nodules containing 65 per cent. lead-oxide; these, however, are nothing but a basic acetate of lead. (Pasteur.)

Aspartate of Mercury.—Mercuric oxide, boiled with aspartic acid, forms a white powder, containing, when dried at 100°, $2C^4H^6HgNO^4.Hg^2O$, a composition analogous to that of Pasteur's basic lead-salt. (Dessaignes.)

Aspartates of Silver.—When nitrate of silver is added to a slightly alkaline solution of aspartate of ammonium, a precipitate is formed, which disappears on stirring, and the liquid, after 24 hours, yields white, heavy, entangled crystals of a basic salt. The mother-liquor, left to crystallise, deposits yellowish crystals of the normal salt, $C^4H^6AgNO^4$. The basic salt appears to be $C^4H^5Ag^2O^4$. This formula requires 66·86 per cent. oxide of silver, and the mean of several analyses made by different chemists, and not differing by more than 0·2 per cent., gives 66·7 per cent. This salt appears then to be really a dibasic aspartate. Pasteur finds, however, that the same salt, when merely pressed between paper, and then dried for 24 hours at the ordinary temperature, agrees in composition with the basic lead- and mercury-salts, its formula being $2C^4H^6AgNO^4.Ag^2O$. The active and inactive acids yield silver-salts identical in composition. (Pasteur.)

Aspartate (?) *of Ethyl.*—When malate of ethyl is saturated with dry ammonia-gas, the liquid becomes heated, and in a few days solidifies to a radiated crystalline mass, which, after being drained, and then washed with ether, consists of pure malamate (or aspartate) of ethyl, $\left.\begin{matrix} N(H^2.C^4H^4O^3) \\ C^2H^5 \end{matrix}\right\} O$. By further treatment with ammonia, it is converted into malamide [? asparagine]. (Pasteur.)

ASPASIOLITE. A variety of *cordierite* [$3(Mg^2O.SiO^2) + Fe^2O.SiO^2 + 2(2Al^4O^3.3SiO^2)$], in which the magnesia is partly replaced by water. The two minerals crystallise in the same form, and crystals are found consisting partly of cordierite, partly of aspasiolite, the most complete transitions from one to the other occurring in the same specimen. Moreover, both minerals contain the same proportions of silica and alumina; but aspasiolite contains less magnesia and more water than cordierite, the difference being that 1 at. of magnesium in the latter is replaced by 3 at. of hydrogen in the former (or 1 at. of magnesia by 3 at. of water). Similarly it is found that 1 at. of iron or manganese may be replaced by 3 at. H without alteration of crystalline form. This kind of isomorphism, called *polymeric* isomorphism, was discovered by Scherer; it was first noticed in the minerals cordierite and aspasiolite. (Pogg. Ann. lxviii. 319.)

ASPERTANNIC ACID. A variety of tannic acid obtained by Schwartz (Ann. Ch. Pharm. lxxx. 333) to be contained in woodruff (*Asperula adorata*). Schwarz assigns to it the formula $C^{14}H^8O^8$, but it does not appear to have been obtained in a state of purity. (See also Rochleder, Ann. Ch. Pharm. lxxxiii. 64.)

ASPERULA ODORATA. The herb of this plant contains cumarin, aspertannic acid (?), rubichloric acid, citric acid, and probably catechu.

ASPHALT. *Compact Bitumen, Mineral Pitch, Jew's Pitch, Bitumen Judaicum, Judenpech, Erdpech, Bergpech, Goudron minéral.*—A smooth, hard, brittle, black, or brownish-black, resinous mineral, having a conchoïdal fracture, and a streak lighter than the broken surface with which it is made. Specific gravity 1 to 1·68. Odour bituminous, becoming stronger by friction. Melts at about 100° C., easily takes fire, and burns with a bright, but very smoky flame. Like all bituminous substances, it is a product of the decomposition of vegetable matter, consisting chiefly of hydrocarbons, with variable quantities of oxygen and nitrogen, and yields by dry distillation a small quantity of ammoniacal water, a peculiar empyreumatic oil, and a residue of charcoal mixed with variable quantities of inorganic matter. It dissolves partially in alcohol, more easily in oils both fat and volatile; it is also dissolved by alkalis and alkaline carbonates.

Asphalt is found in most parts of the world, sometimes pure, sometimes associated with various minerals. The name *earthy* or *crude asphalt* is applied to various rocks more or less impregnated with bitumen. Pure asphalt is found on the shores of the Dead Sea, issuing from the earth in the liquid state at the bottom, and rising to the surface, where it forms solid lumps, which are thrown upon the shore. In Trinidad there is a lake of bitumen 1½ mile in circumference, cold and solid near the shore, but gradually increasing in temperature and softness towards the centre. Asphalt is also found, more or less pure, in Cuba, South America, and various parts of Europe.

At Seyssel, near the Rhone (Dépt. de l'Ain), it forms a deposit 2500 ft. long and 800 ft. broad, yielding about 1500 tons annually. At Bechelbrunn and Lobsann, in the Lower Rhine, a viscid bituminous mass is found, called *graisse de Strasbourg*, together with a ferruginous sandstone, containing about 12 per cent. of bituminous matter. At Bastennes and Dax, in the Département des Landes, there is a siliceous sand, impregnated with about 6 per cent. of bitumen. In the Val de Travers, Neufchâtel, there is a cretaceous formation, strongly impregnated with asphalt, which is used for building purposes. In the British Isles, asphalt is found at the Poldice mine in Cornwall; near Matlock in Derbyshire; at Haughmond Hill in Shropshire; and at the Hotwells near Bristol; also in limestone near Glasgow; in freestone near Edinburgh; in the sandstone of Caithness; and generally throughout the Orkneys.

Asphalt is separated from the minerals with which it is associated, either by boiling with water, which causes the bitumen to run out in the melted state, or by the action of hydrochloric acid, which dissolves carbonate of calcium and leaves the asphalt, or with oil of turpentine, which dissolves out the bitumen.

The following table contains the results of analyses of various kinds of asphalt: *a* is asphalt from Coxitambo inPeru; *b* from Bastennes; *c* from Pont-du-Château, Auvergne; *d* from the Abruzzi near Naples; *e* from Pontnavey; *f* from Cuba:

	Boussingault.*		Ebelmen.†			Regnault.‡	
	a		*b*	*c*	*d*	*e*	*f*
Carbon	88·63	88·70	78·50	76·13	77·64	67·43	81·46
Hydrogen	9·69	9·68	8·80	9·41	7·86	7·22	9·57
Oxygen	1·68	1·62	2·60	10·34	8·35	23·98	8·97
Nitrogen			1·65	2·32	1·02	1·37	
Ash	—	—	8·45	1·80	5·13	—	—
	100·00	100·00	100·00	100·00	100·00	100·00	100·00

According to Boussingault (Ann. Ch. Phys. [2] lxiv. 141), asphalt or compact bitumen is a mixture of two definite substances, viz. *asphaltene*, which is fixed and soluble in alcohol, and *petrolene*, which is oily and volatile. The greater part of the latter may be volatilised by distilling the asphalt with water.

Petrolene (from the asphalt of Bechelbrunn) forms, when dried over chloride of calcium and rectified, a pale yellow oil having a faint taste and bituminous odour. Specific gravity 0·891 at 21° C. Does not become solid at 12° C. It stains paper, and burns with thick smoke. Boils at 280°, forming a vapour of specific gravity 9·415. It contains, according to Boussingault, 87·2 per cent. carbon and 12·1 hydrogen, agreeing nearly with the formula $C^{20}H^{32}$, which for a condensation to 2 vols. gives the vapour-density 9·5.

Asphaltene is obtained pure by heating asphalt for 48 hours to 250° C., whereby the petrolene is completely volatilised. It is a black solid substance, having a strong lustre and conchoïdal fracture. It becomes soft and elastic at about 300° C., decomposes before it melts, and burns like a resin. It gives by analysis 74·2 per cent. C, and 9·9 H, whence Boussingault deduces the formula $C^{40}H^{32}O^{6}$. Gerhardt prefers $C^{20}H^{32}O^{3}$, and suggests that asphaltene may be formed by the oxidation of petrolene.

Asphalt-oil.—Asphalt yields by dry distillation, a yellow oil consisting of hydrocarbons mixed with a small quantity of oxidised matter. It begins to boil at 90° C. but the boiling point gradually rises to 250°. The portion boiling between 90° and 200° has a specific gravity of 0·817 at 15° C.; that which boils between 200° and 250° has a specific gravity of 0·868 at 15° C. Both portions gave by analysis about 87·5 per cent. carbon, 11·6 hydrogen, and 0·9 oxygen, which is nearly the composition of oil of amber. (Völckel, Ann. Ch. Pharm. lxxxviii. 139.)

Asphalt-oil, treated with nitric acid, is transformed into a resin, having the odour of musk and the taste of bitter almonds. On treating the oil with strong sulphuric acid, part dissolves, while the rest floats on the surface. This latter, when decanted, washed with potash, and rectified, yields an oily mixture, whose boiling point ranges from 90° to 250° C., and density from 0·784 to 0·867 at 15° C. Subjected to fractional distillation at intervals of 20° or 30° C., it yields a number of oils gradually

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* Ann. Ch. Phys. [2] lxxiii. 422. † Ann. Min. xv. 523. ‡ Dingl. polytechn. J. lxviii. 201.

increasing in density, but agreeing very nearly in composition, the mean result of their analysis being 87·5 per cent. carbon, and 12·5 H, a proportion agreeing with the formula $n\mathrm{C}^7\mathrm{H}^6$. It agrees also with Boussingault's analysis of petrolene. All these oils have nearly the same odour, are insoluble in water, but very soluble in alcohol and ether. Strong sulphuric acid scarcely attacks them. They are insoluble in strong nitric acid, and on boiling the liquid, the nitric acid volatilises, and there is formed a very small quantity of a heavy yellow oil.

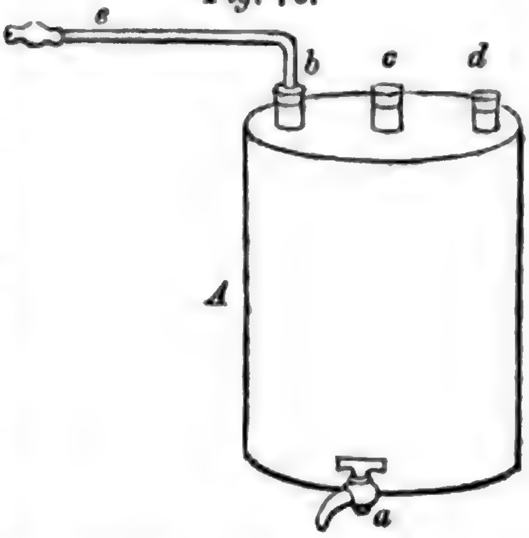
Asphalt was used by the ancient Egyptians in embalming, and appears to have been employed in the construction of the walls of Babylon. It is now used, mixed with sand, chalk, ground sandstone, &c., for pavement, for making water-tight tanks and covers, as a coating for tubes of glass and iron used for conveying gas or water, and for various other purposes of like nature.

Artificial or *Gas-tar Asphalt* is a mixture of sand, chalk, or lime-stone, with the thick pitchy residue obtained by evaporating off the more volatile portions of gas-tar. The mineral substance must be strongly heated to expel moisture and adhering air, the presence of which would prevent the pitch from penetrating thoroughly into the pores of the mineral, and added to the pitch while in the melted state. The pitch should also be very strongly heated, but not enough to char it. This artificial asphalt is used in the same way as the natural asphalt, for pavements, tanks, &c.

ASPHODELUS. The bulbs of *Asphodèle de Sardaigne*, of *Asphodelus racemosus*, and other species of the same genus, are said to contain a fermentable substance from which alcohol may be prepared. According to Landerer, an excellent glue may be obtained from the bulbs of *A. racemosus* and *A. fistulosus* by washing them with water, drying them thoroughly in a stove, grinding them to coarse powder, and mixing the powder with water.

ASPIRATOR. An apparatus first devised by Brunner for drawing a stream of air through a tube or other vessel. The simplest form of it is a cylindrical vessel *A* (*fig.* 76), of zinc or tin plate to hold water, having a cock *a* near the bottom, and three apertures closed with corks *b*, *c*, *d* on the top. *b* is connected with the vessel through which the stream of air is to be drawn; *c* is for the insertion of a thermometer, and *d* to pour in water. The vessel *A* being filled with water, the apertures *c* and *d* closed, and the *cock a* opened, the water runs out; and as air can only enter by the bent tube *e*, inserted into the opening *b*, a stream of air is drawn through the apparatus with which the other end of this tube is connected, the volume of air thus drawn through being exactly equal to that of the water which runs out at *A*. Instead of the metal cylinder, a glass vessel may be used, having a stopcock at the lower part of its side.

Fig. 76.



Regnault, in his analysis of air, used a cylindrical metal vessel with conical terminations, and having at the bottom, a stopcock to which was attached a short glass tube bent upwards, so that the small column of liquid which remained in it when the vessel was emptied of water might prevent air from entering at the bottom The advantage of the conical terminations is that the vessel can be more completely filled and emptied, and the volume of water which runs from it, more exactly measured.

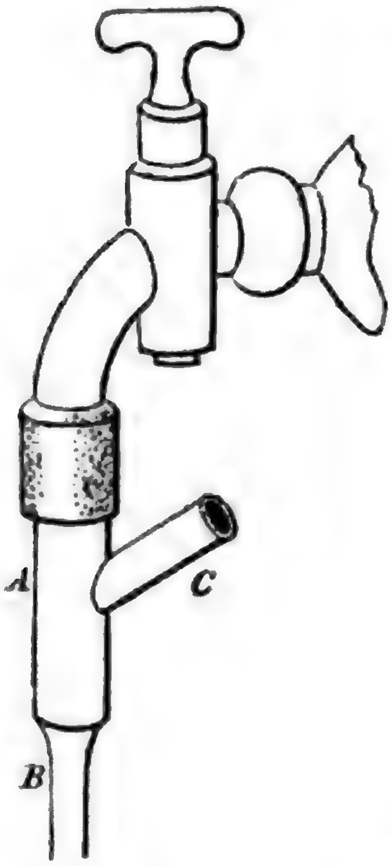
In all these forms of aspirator, the refilling of the vessel with water is very troublesome, especially when large quantities of air are to be drawn through. To obviate this inconvenience, an aspirator has been contrived by Brunner, consisting of two equal cylindrical vessels placed one above the other and communicating by tubes which can be opened or closed, so that, when the water has run from the upper to the lower vessel, the apparatus, turning for the purpose on a horizontal axis, may be inverted so as to bring the empty vessel to the bottom, and the full one to the top; the water may then be again made to run without the trouble of refilling.

Mohr's aspirator has the form of an ordinary gasometer, consisting of two cylindrical vessels, the inner of which, of rather smaller diameter than the outer, is closed at top, and inverted in the outer which contains water. The inner vessel is balanced by a weight passing over a pulley, as in the large gasometers used at gas-works. The vessel through which the air is to be drawn is connected with the inner vessel by a bent tube passing through the outer vessel near the bottom and terminating within the inner vessel.

A simple apparatus, serving both for aspirator and perspirator is described by Dr. F. Guthrie (Phil. Mag. [4] xv. 64).

An aspirator which works by a constant stream of water and does not require any filling or emptying of vessels, has been contrived by M. W. Johnson (Chem. Soc. Qu. J. iv. 186). The principle of this apparatus is the same as that of the water-blast used in the Hungarian mines. The apparatus consists of a small hollow cylinder *A*, of brass or glass, open at both ends, and connected with the vessel through which the air is to be drawn, by the lateral tube *C*. A straight glass tube *B* is fitted to the lower end of the cylinder *A*, and the upper end of that cylinder is attached by a caoutchouc tube to a water-tap supplying a constant stream. On opening the tap, the water, as it runs down, carries the air in the cylinder *A* along with it and the air in the lateral tube *C* is then driven in by the external pressure. In this manner, a stream of air is made to pass from *C* to *A* as long as the water is running. It is best not to open the tap to the full. For a cock $\frac{3}{8}$ of an inch in diameter, the cylinder *A* may be 2 in. long and $\frac{3}{4}$ in. wide; *B* 1 in. long and $\frac{3}{8}$ in. wide; *C* also 1 in. long and $\frac{3}{8}$ in. wide. The volume of air drawn through this aspirator is not equal to that of the water which runs away. With the tube *B*, 8 in. long and $\frac{3}{8}$ in. wide, Johnson found that, for every cubic foot of air drawn in, only 0·69 cub. in. of water was expended. It is clear, therefore, that this form of aspirator cannot be used when the volume of air drawn in is to be exactly measured. In that case one of the aspirators before described must be used. When only small quantities of water are run out, it is sufficient to receive the water in a graduated measure and determine its volume directly. When a large aspirator is used and has to be filled several times, its capacity must be previously determined by filling it with water from a flask of known capacity.

Fig. 77.



This volume of air determined by direct measurement of the water run out, must of course be reduced to the standard pressure and temperature, 0° C. and 760 mm., the coefficient of expansion for each degree centigrade being 0·003665. A correction is also required for the quantity of aqueous vapour in the air, which is saturated with moisture. To determine the alteration of volume thus produced, we must look in the tables of the tension of aqueous vapour for the tension corresponding to the observed temperature. Let this tension expressed in millimetres of mercury be f; also let h denote the height of the barometer, t the temperature in centigrade degrees; v the observed and v' the corrected volume of the air: then

$$v' = v . \frac{h - f}{760} . \frac{1}{1 + 0{\cdot}003665 . t}$$

ASSACOU or **USSACU.** The Brazilian name for the *Hura brasiliensis Martius*, a euphorbiaceous tree, the bark and sap of which contain an acrid very poisonous principle. The thickened sap and the decoction of the bark exert an emetic action, produce ulcerating pustules on the skin, and are used as a remedy for elephantiasis. The natives also use them to prepare poisonous drinks, against which no antidote is known. (Mérat and Gilbert, Pharm. Centr. 1849, p. 30.)

ASSAMAR. (From *assare* to roast, and *amarus* bitter.) This name was given by Reichenbach to the peculiar bitter substance produced when gum, sugar, starch, gluten, meat, bread, &c. are roasted in the air till they turn brown. Reichenbach (Ann Ch. Pharm. xlix. 3) prepares it by roasting thin slices of bread till they become black-brown, treating the pulverised product with absolute alcohol, evaporating to a syrup, again treating with alcohol, &c. till a residue is obtained completely soluble in alcohol. The alcoholic solution is then mixed with ether, which precipitates a peculiar brown substance; the decanted liquid is evaporated; and the residue carefully heated till it is dry. Völckel (Ann. Ch. Pharm. lxxxv. 74) prepares assamar in a similar manner, from the brown tarry liquid obtained by the dry distillation of sugar or caramel, after neutralising the acid contained in the liquid with carbonate of sodium, and evaporating.

Assamar, according to Reichenbach, is a yellow transparent solid; but according to Völckel, it is a reddish-yellow syrupy liquid, which does not solidify till it begins to decompose. It is extremely hygroscopic, and dissolves in water in all proportions. When heated, it melts (Reichenbach), becomes more fluid, and at 100° C., decomposes and becomes darker in colour, after which it no longer dissolves completely in water (Völckel). The aqueous solution is neutral, and reduces nitrate of silver when heated. Assamar is dissolved by potash, and acids precipitate from the solution, a body of different composition. Völckel assigns to assamar the formula $C^{24}H^{12}O^{12}$; but it is doubtful whether the substance so-called is a definite compound, or has ever been obtained in the pure state.

ASTER-TRIPOLIUM. *Sea Starwort.*—The ash of this plant, which grows in salt-marshes, is very rich in chloride of sodium. The several parts of the plant gathered towards the end of September, were found by Harms (Ann. Ch. Pharm. xciv. 247) to yield ash of the composition and amount given in the following table:

	Root-leaves.	Stems.	Stem-leaves.	Flowers.
Ash per cent	14·9	8·7	16·2	9·4
Containing, in 100 pts., after deducting charcoal and sand:				
Carbonic acid (anhyd.)	3·4	3·3	4·2	3·7
Sulphuric acid (anhyd.)	2·7	1·8	4·1	10·5
Phosphoric acid (anhyd.)	2·0	0·6	1·7	10·8
Silica (anhyd.)	0·6	0·5	0·8	1·0
Chloride of sodium	65·5	68·5	60·2	30·0
Chloride of potassium	3·7	14·1	—	—
Soda	—	—	14·0	1·4
Potash	13·6	2·5	6·1	25·4
Lime	5·0	4·5	4·8	7·2
Magnesia	2·2	2·2	1·7	5·7
Sesquiphosphate of iron	1·1	2·1	2·3	4·0
Manganaso-manganic oxide	trace	trace	trace	trace

ASTRACAMITE. A native sulphate of magnesium and sodium, $SO^4MgNa.2H^2O$ occurring in white, opaque, prismatic crystals, together with ordinary sulphate of magnesium, in the bitter salt-marshes on the eastern side of the mouth of the Volga.

ASTRALITE. A glass flux resembling aventurin, but containing crystals of a cuprous compound, which by reflected light exhibits a dichroitic iridescence of dark red and greenish-blue. To prepare it, a mixture of 80 pts. of silica, 120 lead-oxide, 72 carbonate of soda, and 18 anhydrous borax, is fused either with 24 pts. of scale oxide of copper, and 1 pt. of scale oxide of iron, or with 5 pts. of lime, 26 scale oxide of copper, and 2 scale oxide of iron. The mixture is fused in a hessian crucible, at the heat of an ordinary air-furnace, and left to cool slowly in the furnace. The first mixture melts more easily than the second, and yields larger crystals. The dichroitic iridescence is particularly beautiful on cut and polished surfaces. (Pettenkofer, Abhandl. d. naturw. techn. Commission bei d. Akad. d. Wiss. zu München, p. 134.)

ASTROPHYLLITE. A variety of mica found at Brevig in Norway. It contains silica, alumina, ferric oxide, magnesia, potash, soda (a trace), ferrous oxide, manganous oxide, lime, and about 3 per cent. of water. The amount of iron is unusually large. Fluorine is absent. Before the blowpipe it melts easily, and with intumescence. Colour pinchbeck-brown, varying to nearly a golden-yellow in the thinner parts. The crystals are often united in beautiful stellate and floral groups: hence the name. (Scheerer, Berg- u. hüttenmannische Zeitung, 1854, s. 240.)

ATACAMITE. A native oxychloride of copper, originally found in the desert of Atacama in Peru, and since observed in other localities, viz. in some silver mines in Peru, in the districts of Huasco Bajo and Aconcagua in Chili, in the lavas of Vesuvius, and in the mines of Schwarzenberg in Saxony. According to the analyses of Klaproth, J. Davy, Ulex, and Mallet, it contains $CuCl.3CuHO$, or $CuCl + 3(CuO.HO)$. Berthier (Rammelsb. Handw. i. 55), found in a specimen from Cobija, twice the amount of water given by the above formula. F. Field (Chem. Soc. Qu. J. vii. 194), deduces from his analysis of a specimen from Copiapo in Chili, the formula $CuCl + 3CuO + 5HO$, or $CuCl.3CuHO.H^2O$. It forms small rhombic crystals, varying in colour from leek to emerald green, and generally aggregated in crystalline groups. According to Monteiro (Phil. Mag. [4] xiii. 470), it occurs at Serra do Bembe near Ambriz, on the west coast of Africa, in small translucent crystals, $\infty P . \breve{P}\infty$, on malachite and quartz. It dissolves easily and completely in acids, and in ammonia. It is used for the extraction of copper.

ATHAMANTA OREOSELINUM. The root and seeds of this plant contain a peculiar bitter substance, not yet examined, together with athamantin (see next article). The leaves contain, not athamantin, but a bitter principle and a volatile oil, which is obtained by distilling the herb with water. This oil has the composition of oil of turpentine, $C^{10}H^{16}$; it smells like elder, has a density of 0·841, and boils at 163° C. With hydrochloric acid gas, it forms an uncrystallisable liquid, which is colourless after distillation, lighter than water, and boils at 190° C. It does not appear to be related, in composition or properties, either to athamantin or to oil of valerian, which is produced by the decomposition of the latter. (Schnedermann and Winckler, Ann. Ch. Pharm. li. 336.)

ATHAMANTIN. $C^{24}H^{30}O^7$. (Gm. xii. 101; Gerh. iv. 269.)—A substance existing in the root and seeds of *Athamanta oreoselinum*, and other species of the same genus. It was first obtained in an impure state by Winckler (Buchn. Repert. xxvii. 169), afterwards prepared pure and more completely examined by Schnedermann (Ann. Ch. Pharm. li. 315). It is extracted by treating the roots and seeds with alcohol. The solution, if not too concentrated, yields the athamantin, by spontaneous evaporation, in crystals, which may be purified by pressure and recrystallisation. It forms colourless, fibrous, silky crystals, or sometimes rectangular prisms with truncated summits; has a rancid soapy odour, and a slightly bitter acrid taste. It is insoluble in water, and melts in it at the boiling heat, in drops which sink to the bottom of the vessel. It dissolves readily in alcohol and ether, and the solutions are not precipitated by metallic salts. It melts between 60° and 80° C. It does not volatilise undecomposed, although it can sustain a tolerably high temperature without decomposition. By dry distillation, it yields valerianic acid and other products.

Melted athamantin absorbs hydrochloric acid gas, and appears to enter into combination with it, but on raising the temperature to 100° C., decomposition takes place, and the athamantin is resolved into valerianic acid and oreoselone:

$$\underbrace{C^{24}H^{30}O^7}_{\text{Athamantin.}} = \underbrace{2C^5H^{10}O^2}_{\substack{\text{Valerianic}\\ \text{acid.}}} + \underbrace{C^{14}H^{10}O^3}_{\text{Oreoselone.}}$$

When hydrochloric acid gas is passed into an alcoholic solution of athamantin, the products formed are oreoselone and valerate of ethyl. Sulphurous acid acts on athamantin like hydrochloric acid, a crystalline compound being formed at first, and soon afterwards oreoselone, valerianic acid, and sulphurous acid gas. Concentrated sulphuric acid dissolves athamantin and decomposes it in like manner. Athamantin heated with caustic potash, yields valerate of potassium, and a white amorphous substance, which appears to be a hydrate of oreoselone. Lime-water and baryta-water act in the same manner, but more slowly. (See OREOSELONE and PEUCEDANIN.)

Trichlorathamantin, $C^{24}H^{27}Cl^3O^7$, is a light yellow resinous body, produced by mixing an alcoholic solution of athamantin with water, and cautiously adding dilute chlorine-water, till the liquid smells slightly of chlorine. A corresponding bromine-compound appears to be formed by treating athamantin with bromine-water.

Trinitrathamantin, $C^{24}H^{27}(NO^2)^3O^7$, is formed, together with other substitution-products, by the action of cold fuming nitric acid on athamantin. Precipitated by water, it is a yellow pulverulent substance, scarcely wetted by water, easily soluble in alcohol, ether, and ammonia, slightly in dilute nitric acid. (Geyger, Ann. Ch. Pharm. cx. 359.)

ATHANOR or **ACANOR.** *Piger Henricus*, *Fourneau des paresseux*.—A kind of furnace, which has long since fallen into disuse. The long and tedious operations of the ancient chemists rendered it a desirable requisite, that their fires should be constantly supplied with fuel in proportion to the consumption. The athanor furnace was peculiarly adapted to this purpose. Beside the usual parts, it was provided with a hollow tower, into which charcoal was put. The upper part of the tower, when filled, was closely shut by a well-fitted cover; and the lower part communicated with the fire-place of the furnace. In consequence of this disposition, the charcoal subsided into the fire-place gradually as the consumption made room for it; but that which was contained in the tower was defended from combustion by the exclusion of a proper supply of air. U.

ATHAR or **ATTAR.** The Indian name of volatile oil of roses.

ATHERIASTITE. The name given by Weibye to a mineral from Arendal, bearing an external resemblance to scapolite. In composition it appears to be related to epidote, as will be seen by the following comparison of its analysis by Berlin (Pogg. Ann. lxxix. 302) with that of epidote from Arendal by Scheerer (*ibid.* xcv. 503).

	Atheriastite.	Epidote.
Silica	38·00	37·59
Alumina	24·10	20·73
Ferric oxide	6·22	16·57
Lime	22·64	22·64
Magnesia	2·80	0·41
Water	6·95	2·11
	100·71	100·05

Berlin does not state whether the iron in atheriastite is present as a ferrous or as a ferric compound; but it is probably all in the form of ferric oxide. (Scheerer, Handw. d. Chem. 2^{te} Aufl. i. 405.)

ATLAS ORE. See Malachite.

ATLAS SPAR. See Satin Spar.

ATMERYTHRIN. The name given by Kane (Compt. rend. ix. 656) to a product which volatilises in red vapours, and condenses in reddish-green laminæ, in the dry distillation of litmylic acid (erythrolitmin) and litmic acid (a mixture of azolitmin and spaniolitmin), with lime.

ATMIDOSCOPE. An instrument invented by Babinet (Compt. rend. xxvii. 529) to measure the rate of evaporation.

ATMOSPHERE. The gaseous envelope which surrounds any solid or liquid body is called an atmosphere (ἀτμὸς smoke, σφαῖρα globe); thus we speak of the atmosphere of oxygen which spongy platinum attracts to its surface, or of the reduction of a metal in an atmosphere of hydrogen. The term atmosphere is, however, especially employed to designate the gaseous matter which encircles the solid and liquid portions of the earth's surface, forming the air or earth's atmosphere.

Of the existence of matter above the visible crust of the globe we have striking evidence in the resistance offered to bodies moving near the earth's surface and in the effects produced by wind; but the most direct proof that the air is attracted by the solid and liquid portions of the earth's body, or that the air has weight, is afforded by the fact that a vessel filled with air weighs more than the same vessel from which the air has been removed, and that a closed vessel filled with air weighs less in the atmosphere than it does in a vacuum. That the air possesses weight was suspected even before the time of Aristotle; but Galileo, in 1640, was the first who gave the right explanation to the fact observed by the Florentine pump-makers, that they were unable to raise water by a suction-pump more than 32 feet, and supposed by them to show that nature had a "horror vacui." Galileo's explanation was beautifully verified by his pupil Torricelli, who argued that, if the atmospheric pressure supports a column of water 32 feet in height, it must support a column of mercury, which is nearly fourteen times heavier than water, of about 30 inches in height; and thus the first barometer was constructed, the empty space above the mercury in the tube being called, from its discoverer the, *Toricellian vacuum*.

The atmosphere, then, having weight, or obeying the laws of gravitation, forms a part of the earth's body, and accompanies the solid and liquid portions in their axial and orbital motions. The height to which the atmosphere extends above the earth's surface is not the same at all points, since, owing to the increase of the attractive force at the poles and its diminution at the equator, and to the action of the centrifugal force, as also to the increase of temperature, the atmosphere presents, like the earth's solid body, the form of a spheroïd, whose polar is considerably shorter than its equatorial diameter. The absolute height to which the atmosphere extends above any point on the surface of the earth has not been determined with any degree of certainty: for, as air is an expansive fluid, and the volume which a given quantity of air occupies is directly dependent upon the pressure and temperature to which it is exposed (in accordance with the known laws regulating the expansion and contraction of gases), the density of the atmosphere is not uniform, but diminishes as the distance from the earth's surface increases: the exact point at which the atmosphere terminates is thus very difficult to determine. That there is, however, a limit of the earth's atmosphere is rendered certain from the fact, ascertained by the observations of the occultations of stars or satellites, that our moon and most of the planets are destitute of an atmosphere like ours, which could not be the case if the terrestrial air were diffused throughout space. Dr. Wollaston supposed that a gas cannot expand beyond a certain limit, and Faraday has shown that in the case of the vapour of mercury such a limit really exists: hence there can be no doubt that there is a definite limit to the atmosphere; and, from calculations of the time during which the twilight extends to the zenith, it appears that the atmosphere reaches, in a state of sensible density, to the mean height of from forty to forty-five miles above the earth's surface.*

Barometric observations at various heights above the sea-level prove conclusively that Galileo's theory of atmospheric pressure is correct. The first of these barometric measurements, made on the Puy-de-Dôme by Pascal's advice in 1648, showed that the column of mercury supported by the atmosphere sinks as the distance from the earth's surface increases; thus, at the sea-level, the mean height of the barometric column is 760 millimetres (29·92 English inches), whereas in Potosi, at a height of 13,220 feet, the mercury sinks to a mean level of 471 millimetres. The average weight, then, of the atmosphere at the level of the sea is, in our latitudes, that of a column of mercury 760 mm. in height, or equal to a pressure of 103·33 kilogrammes on a square decimetre (nearly 15 pounds on a square inch). This weight, the human body, in common with all substances existing at the bottom of the ocean of air, has to carry; and although it may at first sight appear remarkable that the animal frame should be able without discomfort to bear a pressure amounting to several tons, yet it is certain that not only is this the case, but that our bodies are arranged so that we cannot exist without this pressure; and as an effect of the weight of the air, it has been shown by the brothers Weber, that the human thigh-bone is, in certain positions of the body, retained in its place, together with the ball and socket hip-joint, only by atmospheric pressure; it is well known also that persons remaining for any length of time at great heights above the earth's surface are inconvenienced by hæmorrhage from the nose, eyes, and mouth, owing to the small blood-vessels, unsupported by the atmospheric pressure, being unable to withstand the forcible propulsion of the blood through the system.

The relation according to which the density of the air diminishes in ascending, is easily deduced from the well-known law of Mariotte, that the density of a gas is directly proportional to the pressure to which it is subject; whence it follows that, alterations of temperature and variations in the force of gravity at different heights not being considered, the density diminishes in a geometrical ratio, as the height increases in an arithmetical ratio. It has been found by experiment that, when the barometer stands at a height of 760 mm. it is necessary to ascend 10·5 metres in order to effect a fall of 1 millimetre in the barometric column, or to bring the mercury to stand at 759 mm., or at $760 \cdot \frac{759}{760}$ mm. Now we may assume, without appreciable error, that the air throughout this space of 10·5 metres is of equal density; at a height, then of 10·5 metres the pressure is $760 \cdot \frac{759}{760}$: hence the air in the next 10·5 metres has only a density of $\frac{759}{760}$ of what the lower layer had; and therefore, in ascending through the second 10·5 metres, the barometer does not fall 1 millimetre, but only $\frac{759}{760}$ of a millimetre, so that at a height of twice 10·5 metres, the barometer will stand at $760 \cdot \frac{759}{760} - \frac{759}{760} = 760 \cdot \left(\frac{759}{760}\right)^2$; and as the density of the third layer of 10·5 metres is $\frac{759}{760}$ times less than that of the second, the barometer at the height of three times 10·5 metres, will be $760 \cdot \left(\frac{759}{760}\right)^2 - \left(\frac{759}{790}\right)^2 = 760 \cdot \left(\frac{759}{760}\right)^3$, and so on. If, then, at two places the barometer stands respectively at $B = 760 \cdot \left(\frac{759}{769}\right)^n$ and $B' = 760 \cdot \left(\frac{759}{760}\right)^m$, their difference in elevation is $10{\cdot}5\,\text{m} \times (n - m)$; hence, from these two equations the difference in height, H, between these two points expressed in metres is

$$H = 18363\,(\log B - \log B')$$

or in English feet

$$H = 60246\,(\log B - \log B').$$

By means of this formula, we find that the pressure is diminished to half its original amount, and therefore the air expanded into double its original volume, at a height of 5528 metres or 18,136 ft. above the level of the sea, and that at a height of twice 5528 metres, the pressure is reduced to ¼ of its original amount, and so on.

The mean temperature of the atmosphere, like its density, is not equal throughout the mass, but diminishes as the distance from the earth's surface increases, so that, at a certain height above the sea-level, different for different latitudes, we arrive at a

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* In order to give an idea of the relation between the earth's diameter and the height of the atmosphere, it may be stated, that if we represent the earth by a globe of 1 foot in diameter, the atmosphere will be represented by a layer of air $\frac{1}{15}$ of an inch in height.

line above which the mean temperature of the air does not rise higher than the freezing point, and this line is called the level of perpetual snow. This regular diminution of temperature in the higher regions of the atmosphere is to be attributed mainly to two causes: 1st, to the fact that the air absorbs but a small portion of the heating rays of the sun in their passage to the earth, the lower zones of the atmosphere being heated by contact with the warmer solid and liquid crust of the globe; and, secondly, to the increase of latent heat which all gases undergo on rarefaction, producing a diminution in temperature. Besides this regular alteration of mean temperature of the various zones of air above the earth, the various portions of the atmosphere exhibit great and constant variation in temperature, owing to the unequal heating effects produced by the sun on the earth in various latitudes and at various times. The mean temperature of any place, and therefore of the air above that place, is the resultant of the amount of heat received from the sun, and that lost by radiation. These two controlling causes are, however, never constant, either in the same or in different places, and hence the temperature is continually varying. The chief factor representing the change of temperature, is the height to which the sun rises above the horizon, and the intensity with which any point on the earth's surface is heated, is proportional to the cosine of the sun's zenith-distance at that point; thus, in the torrid zone, the sun's zenith-distance varies from 0° to 33°·5, or the cosine from 1 to 0·917, whilst in the temperate and frigid zones the cosine of the angle varies from 0·930 to 0·367, and from 0·731 to 0. We see from these numbers that, although many other circumstances, such as duration of day and night, and the thickness of atmosphere through which the sun's rays have to pass affect the temperature, the warm climate of the torrid zone is not subject to such variations as occur in the other portions of the globe. The height at which the mean atmospheric temperature sinks below 0° C., or the height of the snow-line, in different latitudes, is determined by many circumstances besides those already mentioned, as, for instance, the geographical relations of the country, neighbourhood of large masses of water, &c.; thus the snow-line on the northern slope of the Himalaya is found at a height of 15,600 ft., whilst on the southern slope it reaches only 12,200 ft. above the sea. Still the general descent of the line of perpetual snow with increase of latitude is, notwithstanding these local irregularities, plainly seen; thus, under the equator, the snow line is not reached until 15,207 ft., whereas, under the latitude of 60°, it is found at 3818 ft., and in latitude 75°, at only 1016 ft. above the sea-level.

In passing through the atmosphere, a portion of the solar rays is absorbed, the amount of this absorption depending upon the thickness of the layer of air through which the rays pass. Pouillet (Pogg. Ann. xlv. 25 and 481) concluded, from his own experiments, that when the sun is in the zenith and the atmosphere clear, the amount of the sun's heat which is absorbed by passing through the air, varies from 18 to 25 per cent. of the quantity which enters the atmosphere.

The light of the sun is also partially absorbed and reflected in its passage through the air, and, according to Clausius (Pogg. Ann. lxxii. 294), out of 1000 rays of direct sunlight entering the atmosphere, 750 reach the earth direct, whilst 186 are reflected as diffuse light, and 64 are absorbed. For the more refrangible chemically active rays, Bunsen and Roscoe have lately determined the amount of atmospheric absorption and reflection: for the numerical results of these experiments the reader is referred to the article on the Chemical Action of Light. Besides suffering absorption and reflection, every ray of light which enters the atmosphere otherwise than perpendicularly to the limiting surface, undergoes refraction, or is bent out of its course in the direction of the denser medium, so that, as we see the object in the direction of the tangent to the curve as it enters the eye, all celestial objects appear higher than they really are. According to the experiments of Biot and Arago, the refractive index, from the absolute vacuum into air at 0° C. and 0·76 m. pressure of mercury, is 1·000294; and hence the refractive power of the air is equal to 0·000588.*

Owing to the unequal heating effect which the sun produces on the various portions of the earth's surface, either from general or local causes, the temperature of the atmosphere varies in every part of the globe, and in the same part undergoes continual change, thus producing the motion of masses of air which we call wind. Winds are invariably caused by the ascent of a heated mass of air, and the motion of a colder mass to fill up the space thus left vacant; the former of these gives rise to currents in the higher regions of the atmosphere, whilst the latter produces the horizontal currents which we observe at the surface of the earth. Winds may either be confined to very narrow limits, as for example the sea and land breezes seen on every coast, or they may extend over a large portion of the globe, as is the case with the trade winds. The former are caused by local circumstances depending upon the unequal heat-absorb-

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* *If the index of refraction be = n, the refractive power is n^2-1. See* LIGHT.

ing and radiating power of the sea and land, whilst the latter depend upon the unequal distribution of temperature throughout the globe, being caused by the rise of hot air from the equatorial zones, inducing horizontal currents to stream in from the colder polar regions. These polar currents would, if the earth were at rest, move directly south and north to the equator; but, owing to the earth's axial motion from west to east, they pass continually over latitudes having a velocity of rotation greater than that of the current, which therefore acts as a resistance towards the east, or as a north- or south-east wind.

Composition of the Atmosphere.

It was not until the year 1774 that the true composition of the atmosphere was pointed out by **Lavoisier**. Before this time, the air was spoken of as one of the four elements, together with fire, earth, and water; and it was only during the few years preceding this date that the vague impressions of speculative philosophers were exchanged for the careful observations of Priestley and Scheele, whose discovery of oxygen had paved the way for the knowledge of the exact composition of the atmosphere. In November 1774, having the advantage of acquaintance with Priestley's previous discovery of the vital air procured from red precipitate, Lavoisier announced to the world that the atmosphere consists of two gases, one of them being essential to life, and the other incapable of supporting respiration or combustion. These two gases he named *oxygen* (ὀξὺ, acid, and γεν to give rise to) and *azote* (α privative, and ζωὴ, life) or *nitrogen*, and he found that the first of these gases occupies about one-fifth by bulk of the atmosphere, the other occupying the remaining four-fifths. Besides these two gases, which form by far the largest portion of the atmosphere, many other substances occur in the air, which although present in comparatively small quantities, play so important a part in the action of the atmosphere on our globe that they cannot be regarded as accidental constituents: these substances are, *aqueous vapour*, *carbonic acid*, *ammonia*, and *organic decomposing matter*. The atmosphere also contains traces of very many other bodies which may be considered as foreign or accidental constituents, such as nitric acid, sulphurous acid, carbonic oxide, hydrocarbons and minute solid particles which are seen floating about in the air by the light of a sunbeam.

Since the time of Priestley, Scheele, and Lavoisier, the determination of the quantitative composition of the atmosphere has been made the subject of experiment by many of the most eminent chemists of the present century; but in spite of these numerous investigations, the relative distribution of the component gases of the atmosphere is still but imperfectly known.

At the commencement of this century, there was much difference of opinion amongst scientific men as to the true composition of the atmosphere: Prout, Döbereiner, and Thomson considered the atmosphere to be a chemical compound of 20 volumes of oxygen, and 80 volumes of nitrogen, whilst **Dalton** (Manchester Memoirs, 2 Ser. vol. i. p. 244) contended that the atmosphere is a mere mechanical mixture, but supposed that the relative amounts of the two gases varied according to their specific gravities at different heights above the earth's surface, the oxygen increasing in quantity the nearer the sea-level was approached, and the amount of nitrogen becoming larger as the distance from the surface of the earth increased.

That the determination of the amount of **oxygen** which air in different localities contains, should have excited the interest of men of science as soon as the discovery of the true composition of the air was made, does not seem remarkable, when we bear in mind the direct dependence of all life upon this element, and the great influence which even slight alterations in the amount of atmospheric oxygen might produce on the animal life subjected to this change, and hence Eudiometry (εὔδιος, good, εὐδία, serene air, and μετρεῖν, to measure), or the mode of measuring the quality of the air, quickly became a new and important branch of chemical analysis. At first sight it appeared not unlikely that the unequal development of animal life on the various parts of the globe, would effect considerable alterations in the composition of the air in different localities; and this idea was borne out, not only by the well-known fact of the unhealthiness of the air of certain districts, such as crowded towns, marshes, and the like, but also by the earliest determinative experiments, which showed variations in the composition of air of various localities amounting to nearly 10 per cent. Thus Fontana determined the quantity of oxygen contained in air by absorption with nitric oxide, and obtained results showing from 18 to 25 per cent.; whilst Scheele, on absorbing the oxygen with sulphide of potassium, or by a mixture of sulphur, iron, and water, found from 25 to 33 per cent. of that gas present in air. Other experimenters, however, and among them Dalton, Gay-Lussac, Davy, and Boussingault found, on employing other analytical methods, that the amount of the atmospheric oxygen varied but very slightly in different situations, and that the non-accordance of the results formerly obtained was owing to errors of experiment, caused by the use of imperfect methods. The quantity of oxygen found by Dalton in English air was from 20·7 to 28 per cent., and Gay-Lussac and Humboldt found that Paris air contained from 21·1 to 20·9 per cent., whilst Davy in London obtained from 20·8 to 21·1 per cent.; Thomson in Glasgow, 21·1; and Kupffer, in Kasan, 21·1 per cent. of oxygen. Experiments made by Dalton himself on the composition of mountain air, did not tend to confirm his theory as to the diminution of the relative quantity of oxygen at great heights; and further experience showed that Dalton's views, although theoretically correct for an atmosphere of mixed gases at rest, are not applicable to the air in motion: for Gay-Lussac and Thénard analysed the air which the former savant collected in his celebrated balloon ascent at a height of 7000 metres, and they found that the oxygen amounted to 21·6 per cent. agreeing exactly with an analysis of the air of Paris, made in the same way at the same time, both differing, however, owing to a common error of experiment, from the exact result of later observers. Although from these experiments we can draw the important conclusion that, within certain very small limits, the air has throughout its mass a constant composition as regards oxygen, still the observational errors of these earlier investigators were large, and it was evidently necessary that the composition of the atmosphere should be determined with all the precision that modern science could bestow. The more recent labours of Dumas and Boussingault, Regnault, Bunsen, and Lewy, have attained this end by help of methods in which the maximum error is reduced to $\frac{1}{5000}$.

The analysis of air may be conducted in two ways. Either by measuring the volumes of the component gases, or by determining their weight. The details of the former, or the eudiometric method, are fully described in the article on ANALYSIS OF GASES, and this is the method adopted, with slight variations, by Regnault, Bunsen, and Lewy, whilst the determination by weight has been employed by Dumas and Boussingault.

For the purpose of carrying out the analysis of air, these two French chemists [Ann. Ch. Phys. [3] iii. 257], employed an apparatus in which air previously freed from aqueous vapour, carbonic acid, and ammonia, by passing through U-tubes containing sulphuric acid and potash, was passed through a weighed tube containing metallic copper kept at a red heat, and then entered an exhausted balloon, the weight of which had been accurately determined. The difference of weight of the tube before and after the experiment, was due to the oxygen; that of the balloon, to the nitrogen of the air which passed into the apparatus. This process, conducted with every possible precaution, showed the composition of the atmosphere to be:

	Percentage of oxygen by Weight.	
1841.	Small balloon.	Large balloon.
27th April	22·92	22·92
28th „	23·03	23·09
29th „	23·03	23·04
	22·993	23·016

or 100 parts by weight of air, are composed of 23 parts of oxygen, and 77 parts of nitrogen. From this composition by weight, the composition by volume of the air can be determined when the specific gravity of the oxygen = o and that of the nitrogen = n are given: for $\frac{23}{o} + \frac{77}{n} = \frac{100}{1}$. Dumas and Boussingault found, on employing the specific gravities as obtained by Berzelius and Dulong, that the sum was not 100 but 99·76; hence they concluded that these specific gravities must be incorrect, and determined them again, obtaining o = 1·1057, and n = 0·972, from which the composition by volume of the atmosphere was found to be

$$\begin{array}{lcr} \text{Oxygen} & = & 20{\cdot}81 \\ \text{Nitrogen} & = & \underline{79{\cdot}21} \\ & & 100{\cdot}02 \end{array}$$

The near approximation of these numbers to the truth, has since been proved by the very exact experiments of Regnault (see Regnault's work on Steam, p. 151; or Pogg. Ann. lxxiv. p. 202), who has shown that one litre of air at 0° C. and 0·76 m. pressure, freed from moisture, carbonic acid, and ammonia, weighs 1·293187 grms., whilst one litre of oxygen, under like circumstances, weighs 1·429802 grms., or has a specific gravity of 1·10563, and 1 litre of nitrogen at 0° C. and 0·76, weighs 1·256167 grm., or has a specific gravity of 0·97137. In accordance with these results, Boussingault found in air which he collected in South America, the following percentage volumes of oxygen:

Air from Santa Fé de Bogota,	at a height of	2650 m.	above sea-level	20·65 p. c. O.
„ Ibaqué	„ „	1323	„ „	20·70 p. c. O.
„ Mariquita	„ „	548	„ „	20·77 p. c. O.

The eudiometric determinations of Bunsen and Regnault are on the whole to be preferred to any method of analysis of the air by weight, not only from their greater accuracy, but from the simplicity of the apparatus employed, and the ease with which small samples of air collected at various times and in different localities can thus be analysed.

Bunsen (Gasometry, p. 71), in a series of analyses of air made on fourteen different days in January and February 1846, amongst which the maximum amount of oxygen was 20·97 per cent. and the minimum 20·84 per cent., found a mean of 20·93 per cent. of oxygen.

Regnault (Ann. Ch. Phys. [3] xxxvi. 385) has analysed a very large number of samples of air collected in various quarters of the globe in a uniform manner, according to instructions given by him. The method of analysis employed rarely gave a difference of 0·02 per cent. on the same sample of air. In more than one hundred analyses of air collected in or near Paris, Regnault found a maximum amount of 20·999 vols. of oxygen, and a minimum of 20·913 or a mean of 20·96. This difference of 0·086 per cent. is, according to Regnault, too large to be accounted for by experimental errors.

9 samples from Lyons, Montpelier, Normandy gave from	20·918 to 20·966	p.c. of O.
30 samples collected in Berlin contained . . .	20·908 „ 20·998	„
10 „ „ Madrid „ . . .	20·916 „ 20·982	„
23 „ from Geneva and Chamounix . . .	20·909 „ 20·993	„

Of seventeen samples of air collected in Toulon Roads and other parts of the Mediterranean, fifteen gave similar results of 20·912 to 20·982 per cent. oxygen, whilst two samples collected from Algiers harbour contained only 20·42 and 20·395 per cent. This abnormal result cannot be accounted for, but a similar phenomenon was observed by Lewy.

5 samples taken on the voyage from Liverpool to Vera Cruz gave	20·918 to 20·965	p. c. of O.
2 samples from Ecuador in S. America contained .	20·96	„
2 „ the summit of Pichincha, higher than Mont Blanc	20·949 to 20·988	„

Eleven samples collected in the Asiatic seas from 1848 to 1850, all except two, gave normal results. On the 1st February 1849, the air in the Bay of Bengal contained only 20·46 and 20·45 per cent. oxygen, and on the 8th March 1849 the air from above the Ganges, collected during foggy weather, in presence of much decomposing animal matter, temperature 35° C., when cholera was commencing, contained from 20·390 to 20·387 per cent. of oxygen.

Air collected by Captain Sir James Ross in the Arctic seas gave the normal composition from 20·86 to 20·94 per cent. oxygen. The conclusion which Regnault draws from all these determinations, is that the atmosphere shows perceptible, though very small, alterations in the amount of oxygen at different times and in different places. This variation ranges from 20·9 to 21·0 per cent., but from special unknown causes in tropical countries, the amount of oxygen may sink as low as 20·3 per cent. Bunsen's analyses of the air in Iceland confirm these views.

Lewy (Ann. Ch. Phys. [3] xxxiv. 1) has also published a series of analyses of air collected from various parts of the globe. The relative amounts of oxygen and nitrogen were determined by Regnault's eudiometric process, and the maximum difference between the composition of the same sample of air analysed at different times was $\frac{1}{10000}$. The air of Paris contained, in a mean of three experiments, 21·014 per cent. of oxygen, that of Havre 20·888 per cent., whilst that collected on the Atlantic gave 20·961 and 21·061 per cent., and in South America, 20·995 and 21·022 per cent. of oxygen. Hence we can positively state that no greater difference exists between the composition of the atmosphere as regards oxygen and nitrogen in different latitudes (some few special cases excepted), than is found in the same place at different times.

Frankland (Chem. Soc. Qu. J. xiii. 22) has lately determined the composition of air collected by himself at different elevations on Mont Blanc, viz. at the Grands Mulets, at the summit, and at Chamounix. The conclusion which Frankland draws from his experimental numbers is, that as far as the nitrogen and oxygen are concerned, the composition of these samples of air falls within the limits of variation noticed by former experimenters.

That the air is a mechanical mixture and not a chemical combination of oxygen and nitrogen is seen from the following facts: 1. The amounts of oxygen and nitrogen in the air do not present any simple relation to the combining proportions of these elements, and are moreover variable. 2. On mixing oxygen and nitrogen gases in the proportion in which they occur in air, no contraction or evolution of heat is observed, and the mixture acts in every way as air. 3. When air is dissolved in water, the proportion between the oxygen and nitrogen in the dissolved air is quite different from that in the undissolved air, this difference occurring in strict accordance with the laws of the absorption of gases in liquids (see Gases, Absorption of). When water is saturated with air at any temperature below 30° C., 100 volumes of the dissolved air contain 34·19 vols. of oxygen and 65·09 vols. of nitrogen, whilst the undissolved air contains 21·1 per cent. of oxygen and 78·9 per cent. of nitrogen. Were the air a chemical combination of oxygen and nitrogen, such a separation by solution would be impossible.

The other constituents of the atmosphere, viz. the aqueous vapour, carbonic acid, ammonia, and decomposing organic matter, alter in amount at various times and in different places, much more considerably than the oxygen and nitrogen.

The humidity of the air is affected by many circumstances, such as temperature, distance from masses of water, and configuration of the land over which it lies. The amount of aqueous vapour which any volume of air can take up depends entirely upon the temperature of the air, and is represented by the tension and corresponding density of the vapour of water in vacuo for that temperature; thus at 10° C. the tension of aqueous vapour is 9·47 mm. of mercury, and the corresponding density 0·00000974, or 1 cubic metre of air at 10° C. is saturated when it contains 9·74 grms. of water in the form of vapour. It seldom happens, however, that the air contains its saturating quantity of moisture, and the amount varies extremely with the conditions before mentioned; thus, on the coast of the Red Sea, during a simoon, the air was found to contain only $\frac{1}{13}$ part of the aqueous vapour required to saturate it, whilst in our moist climate, the air is often saturated with watery vapour. The following table shows the relative humidity, *i. e.* the existing percentage on the saturating quantity, as found by Kämtz in Halle, as a mean of several years' observations:

Jan.	Feb.	March.	April.	May.	June.	July.	Aug.	Sept.	Oct.	Nov.	Dec.
85·0	79·9	76·4	71·4	69·1	69·7	66·5	61·0	72·8	78·9	85·3	86·2

Hence we see that in Halle the air is most humid in December and driest in August.

The determination of the aqueous vapour contained in the atmosphere may be made, either by leading a known volume of air through weighed tubes containing some hygroscopic substance, as sulphuric acid or chloride of calcium, or by means of hygrometers of various construction, for the description of which the article Hygrometry must be consulted.

The carbonic acid or anhydride contained in the air varies also considerably in amount, though by no means to so large an extent as the aqueous vapour. Many methods are employed for ascertaining the quantity of carbonic acid present in the atmosphere. The most certain method is to absorb the carbonic acid from a known volume of air by passing the air, freed from aqueous vapour and ammonia, through weighed tubes containing caustic potash. Saussure (Pogg. Ann. xix. 391), Brunner (Pogg. Ann. xxiv. p. 569), Pettenkofer (Chem. Soc. Qu. J. x. p. 292), Smith (Chem. Soc. Qu. J. xi. p. 196), and Frankland (Chem. Soc. Qu. J. xiii. 27), have all proposed different methods, for the explanation of which we must refer to the original papers.

From very numerous observations made by Saussure, Brunner, Lewy, and others, it appears that air in the open country contains quantities of carbonic acid varying from 3 to 10 volumes in 10,000 of air. As an average number, it has been found that 4 vols. in 10,000 represent the usual composition of the air as regards carbonic acid. In some few peculiar cases, a much larger proportion of carbonic acid has been found (as noticed by Lewy in S. America at Bogota); but these abnormal results are explained by local circumstances, as neighbouring volcanic emanations or burning forests. The air collected above the ocean showed a small variation in carbonic acid between day and night; that collected in the day contained 5·4, whilst that collected during the night contained 3·3 carbonic acid in 10,000 volumes of air. This observation is easily accounted for by the increase of the coefficients of absorption with the diminution of temperature occurring during the night. Air above the land also slightly changes its amount of carbonic acid at various seasons of the year and times of the day, in dependence upon different meteorological alterations, but as yet experiment has not decided the nature of this dependence. At a certain elevation above the earth's surface, the air, according to Saussure and Schlagentweit, contains more carbonic acid than is found in the lower belts of the atmosphere; this increase, which however is not large, probably arises from the decrease of vegetation in the higher atmospheric regions. In the air of crowded towns or of closed inhabited spaces (such as dwelling-rooms, &c.), the carbonic acid often rises to ten times the normal quantity, owing to inefficient ventilation.

Although the relative amount of 4 vols. of carbonic acid in 10,000 vols. of air appears to be a very small one, yet the absolute quantity of carbon thus contained in the atmosphere is very large, exceeding indeed all that is contained on the earth's surface in the solid form, in the bodies of plants and animals, and that found under the earth's solid crust in the coal formations. The question of change in the composition of the earth's atmosphere as regards carbonic acid is one of vital interest to all forms of terrestrial life: for whilst forming the staple nutriment of the vegetable world, carbonic acid, when present in certain quantities, acts as a violent poison on the higher orders of animal life; nor is the limit at which this gas begins to be hurtful to the animal, very far removed from the quantity which at present exists in the atmosphere: for we find that Leblanc and Péclet assign a limit of five in 1000 (ten times the normal quantity), whilst Reid and Arnott give a much lower limit to the non-injurious effect of this gas. Whether the atmosphere is now slowly undergoing, or has in past ages undergone, any perceptible change in the amount of its carbonic acid, is a question to which, owing to the absence of certain and accurate data, we are as yet unable to give any very satisfactory answer. We do, however, know that there are a great number of causes continually at work, some of which tend to increase the amount of atmospheric carbonic acid, whilst there are others which tend to effect a diminution in this constituent. Whether the resultant of these various counteracting influences is such as to keep, during future ages, the carbonic acid exactly at the present amount, it is, with our present knowledge, impossible to say; but from the remarks which follow, it will be seen that if any alteration occur, it must proceed with extreme slowness.

The principal causes which tend to increase the atmospheric carbonic acid are: (1) The respiration of animals. (2) Combustion of vegetable carbonised material. (3) Exhalations of carbonic acid caused by volcanic and other intra-terrestrial agencies. It would appear that the quantity of carbonic acid escaping from volcanic vents, mineral springs, and other inorganic sources into the atmosphere is much larger than that produced by the two causes first named. According to the calculations of Poggendorff (naturally but very rude approximations to the truth), it seems that, taking the amount of carbonic acid evolved by volcanic action to be ten times larger than that given off by every kind of combustion of carbonised material, the quantity of carbonic acid at present contained in the atmosphere would be doubled in 386 years, supposing, of course, that no causes of diminution of were acting. That such causes of diminution are, however, continually at work we know. They consist mainly in (1) the decomposition of carbonic acid, *i. e.* reduction of carbon and regeneration of oxygen, which living vegetables effect in sunlight. (2) The fixation of carbonic acid as carbonate of lime by the vital action of certain animalculæ, giving rise to coral reefs and islands, and the whole of the vast limestone deposits. (3) The fixation of carbonic acid by inorganic chemical processes.

The immense extent to which these actions, particularly the second one, have gone and are still going on, appears to justify the opinion that if any change in the amount of the atmospheric carbonic acid occur at all, it is more probably a diminution than an increase. Any conclusions which we can draw from geological facts, seem rather to support this opinion: for it is more likely that the air contained a larger amount of carbonic acid during the deposition of the enormous carboniferous system when the vegetation must have been so luxuriant and profuse, and when few, if any, air-breathing animals existed, than less than at present. Still, we have no right positively to assume that the air at the time of the deposition of the coal and limestone contained more carbonic acid than now: for we know nothing of the length of time during which these formations were in progress.

From the foregoing remarks, it is seen that a continual circulation of the atmospheric carbon takes place; the animal gives off the waste portion of its body mainly as carbonic acid, and thus deteriorates the atmosphere, which would soon become unfit for his further use, if the vegetable world did not absorb the poisonous gas, at once retaining the carbon in the solid form, fit for the subsequent nourishment of the animal, and exhaling the oxygen wherewith the higher organism again removes his spent materials.

Having described the causes effecting possible variation of the atmospheric carbonic acid, it is almost needless to consider any change which the oxygen may undergo, for the atmosphere becomes unfit for the sustenance of animal life from the presence of a small quantity of carbonic acid, long before the oxygen is materially diminished. If, however, the carbonic acid is slowly decreasing, it may be interesting to inquire how long our supply of oxygen will last us. Such a speculation has been answered, as satisfactorily as the circumstances admit of, by Dumas and Boussingault. These chemists calculated that if the whole of the earth's atmosphere were put into a balloon and suspended from one end of a balance, it would require 581,000 cubes of copper, each having a side of 1 kilometre (1093 English yards) in length, to be suspended at the other end to equalise the balance. Of this total weight, the oxygen would be represented by 134,000 cubes. Assuming, from the best data, that a man consumes a kilogramme of oxygen per day, taking the population of the earth to be 1000 millions, and supposing that the oxygen taken up by animals and by putrefactive processes is four times as large as that consumed by human beings, and supposing further, that the oxygen given off by plants only covers the expenditure of oxygen effected by other causes not mentioned, it appears, even in this exaggerated case, that an amount of oxygen three times as large as that consumed in one century by the whole number of animals existing on the earth, is represented by 15 or 16 of the copper cubes, each having a side of 1 kilometre in length, or the alteration effected in a century is less than $\frac{1}{8000}$ of the total quantity of oxygen, and is therefore altogether inappreciable by our most exact determinative methods. (See Dumas and Boussingault (1841) Ann. Ch. Phys. [3] iii. 257, 288.)

As regards the ammonia and the organic impurities contained in the atmosphere, we still labour under the disadvantage of insufficient experimental data. The great difficulty in the estimation of these constituents, lies in the very minute quantities which are contained in the atmosphere. This difficulty is seen when we compare some of the statements put forward of the amount of atmospheric ammonia; thus Horsford (Ann. Ch. Pharm. lxxiv. 243), found in 1 million parts of air, 47·6 parts of ammonia, whilst Bineau (Ann. Ch. Phys. xlii. p. 462) found in the same quantity of air, from 0·04 to 0·1 part of ammonia. Between these extremes, we have numerous experiments in which every variation in the quantity of atmospheric ammonia has been found. Although, from the great differences in the numerical results (maximum 135; minimum 0·1 parts of carbonate of ammonia), probably arising, partly from errors of analysis and partly from real variations in the contained quantity, it is impossible to fix upon any number as giving the average composition, still it is certain that the atmosphere always contains ammoniacal salts, and that rain (the first portions more than the latter portions), hail, snow, and dew, all contain appreciable quantities of ammonia.

The atmospheric ammonia plays a very important part in vegetation: for it is mainly if not altogether, from the ammoniacal salts contained in the air, that plants obtain the nitrogen which they require for the formation of seed and other essential parts of their structure. Whether plants are at all able to assimilate the free nitrogen of the atmosphere, must, in spite of the numerous researches on the subject, be considered doubtful. George Ville has for some time asserted, founding his assertion on a large number of elaborate experiments, that plants can absorb and assimilate the free atmospheric nitrogen. Boussingault, on the contrary, from his own extensive investigations, *denies* Ville's conclusions, affirming that it is from nitrogenous compounds alone that plants can assimilate the nitrogen. The commission of the French Academy, which was deputed to examine the question under the direction of Chevreul, reported in Ville's favour, although some doubt as to the estimation of the ammonia contained in the distilled water used, was expressed. Still more lately Lawes, Gilbert, and Pugh, have investigated the subject with great care, and find that plants growing in an atmosphere and on a soil free from ammonia or combined nitrogen in other forms, do not contain more nitrogen than the seeds from which they grow. In the state of uncertainty in which such contradictory statements leave us, we may, however, be certain of one fact in which all the experiments agree, namely, that whether or not plants can assimilate small quantities of free nitrogen, it appears that plants growing in air perfectly free from ammonia, do not flourish to anything like the same extent as plants living in an ammoniacal atmosphere.

Concerning the remaining constituents, and especially the organic putrescent matters, our present knowledge is even less satisfactory or positive than is the case with the ammonia. Within a very recent period, we were unacquainted with any method for determining the presence of organic putrescent matters; and even the very important and ingenious method lately proposed by Dr. R. Angus Smith (Chem. Soc. Qu. J. xi. p. 196) requires much extension and general application before we can arrive at a knowledge of the exact qualitative distribution of the organic impurities. Smith's method (for the details of which we must refer to the paper), depends upon the reducing action which solid, liquid or gaseous organic putrescent matter effects on permanganate of potassium. The strength of the test-solution is determined by adding it to a solution of sugar of known composition, until the colour of the permanganate remains permanent; and the same reaction performed with the air under examination, shows the quantity of contained organic matter. In this way, Smith has detected great differences between the air of various localities. The air from high country ground was found to contain 1 grain of organic matter in 200,000 cubic inches of air, whilst the air from a cesspool contained the same quantity of organic matter in 60 cubic inches of air. In a sanitary, as well as in a purely scientific point of view, it is difficult to over-estimate the importance of this simple method for determining the organic impurities which air contains; and if future research confirm its applicability to all cases, it will prove an invaluable instrument in the hands of the physician and the sanitary reformer.

Besides the constituents already mentioned, air contains minute quantities of **nitrates**, **hydrocarbons**, **sulphurous** and **sulphuric acids**, and according to some chemists, iodine, but this has been lately denied. Ozone also occurs in the atmosphere in very small amounts, varying, however, extremely with the situation and meteorological conditions of the place. (See OZONE.)

The atmosphere of the ocean, as well as of the masses of fresh water occurring on the earth's surface, is subject to the same changes from the existence of animal and vegetable life, as the earth's gaseous atmosphere. The relative proportion between the gases dissolved in the water is fixed in accordance with the law of absorption, and many important and interesting conclusions, such as the relative increase of dissolved oxygen, or diminution of temperature, enabling mammalia to live in the polar but not in the tropical seas, can be drawn from an application of these laws to the atmosphere of the sea. The equilibrium between the constituents of the dissolved atmosphere kept up by animal and vegetable life, is well illustrated by the vivaria now so common, which were first introduced by Mr. Warington.

The air of towns and close-inhabited spaces, becomes, as has been stated, often overcharged with carbonic acid and other impurities. The amount of carbonic acid present in dwelling-rooms, &c., has been made the subject of experiment by Leblanc (Ann. Ch. Phys. [3] v. 223; xxvii. 373), Pettenkofer (Chem. Soc. Qu. J. x. 292); Roscoe (Chem. Soc. Qu. J. x.); and Smith (Chem. Soc. Qu. J. xi. 196). The main results may be stated to be: (1) that in rooms which are not thoroughly ventilated, the amount of carbonic acid may rise from 1 to 7 volumes in 1000 of air; (2) that in well ventilated rooms, the amount of carbonic acid should not rise above 0·8 in 1000; (3) that in ordinary dwellings, or even in school- or barrack-rooms, the carbonic acid is diffused uniformly throughout the space, in whatever parts of the room the exit for deteriorated air is placed, though in the exaggerated case of crowded theatres, the air at the highest part of the building was found to contain more carbonic acid than the air at the level of the stage. For other interesting details, we must refer to the original papers, or to the article on VENTILATION. H. E. R.

ATOMIC VOLUME. *Specific volume; Equivalent volume; Molecular volume.* — The atomic or specific volume of a body is the space occupied by a quantity of it proportional to its atomic weight, and is therefore expressed by the quotient of the atomic weight divided by the weight of a unit-volume, that is by the specific gravity:

$$\text{Atomic volume} = \frac{\text{atomic weight}}{\text{specific gravity}}$$

It must not, however be supposed that the atomic volumes represent the relative volumes of the actual material atoms of different bodies. For, regarding any substance, solid, liquid, or gaseous, as an aggregate of material particles capable of moving amongst themselves, it is impossible to suppose these particles to be in actual contact and to fill up the entire volume of the body; we must suppose them to be separated by certain intervals: consequently the specific gravity, and therefore also the specific volume of the body, will depend, partly on the relative weights of these atoms, partly on the number of them contained in a given space, and therefore on the magnitude of the interstitial spaces. Unless, therefore, the spaces are either infinitely small in comparison with the magnitude of the atoms themselves, or bear the same proportion thereto in all bodies, it is impossible to determine the relative volumes of the actual material atoms: for we have no means of ascertaining the proportion between the size of the atoms and of the intervening spaces in each particular case. The atomic volume of bodies must therefore be understood, as the spaces occupied by aggregates of atoms (including the interstitial spaces), whose weights are proportional to the atomic weights of the bodies.

As the atomic weights, or multiples thereof, represent the proportions in which bodies combine by weight, so likewise do the atomic volumes or multiples thereof indicate the proportions in which they unite by volume, thus: the atomic volume of iodine being $\frac{127}{4 \cdot 95} = 25 \cdot 7$, and that of silver $= \frac{108}{10 \cdot 4} = 10 \cdot 2$, we infer that 25·7 vols. iodine unite with 10·2 vols. silver to form iodide of silver, AgI.

The numbers representing the atomic volumes of bodies vary according to the units of atomic weight and specific gravity chosen, and according to the particular values assigned to the atomic weights. Thus, if the atomic weight of hydrogen be equal to 1, that of chlorine = 35·5, and of sulphur = 32, the atomic weight of hydrochloric acid (HCl) will be 36·5, and that of sulphydric acid (H^2S) = 34. Now the specific gravity of hydrochloric acid gas referred to air as unity is 1·264, and that of sulphydric acid is 1·177. Hence we have:

$$\text{Atomic volume of HCl} = \frac{36{\cdot}5}{1{\cdot}264} = 14{\cdot}44$$

$$\text{,, ,,} \quad H^2S = \frac{34}{1{\cdot}177} = 14{\cdot}44$$

If, on the other hand, we adopt hydrogen as the standard of specific gravity for gases, that of hydrochloric acid is 18·25, and that of sulphydric acid is 17, in each case half the atomic weight. On this hypothesis, therefore, the atomic volumes of both gases are expressed by the number 2. Again, if common ether be represented by the formula $C^4H^{10}O$ [C = 12, H = 1, O = 16], its atomic weight is 74; and, its specific gravity in the gaseous state being 37 (referred to hydrogen), its atomic volume in that state is $\frac{74}{37} = 2$, and in the liquid state (specific gravity at 0° referred to water), its atomic volume is $\frac{74}{0{\cdot}737} = 100{\cdot}41$. But if ether be represented by the formula C^4H^5O [$C = 6$, $H = 1$, $O = 8$], then its atomic volume in the gaseous state will be $\frac{37}{37} = 1$, and in the liquid state $\frac{37}{0{\cdot}737} = 50{\cdot}205$. The atomic volumes of gases and vapours are calculated from the specific gravities referred either to hydrogen or to atmospheric air; those of solids and liquids from the specific gravities referred to water as unity.

Atomic Volumes of Gases.

According to the system of atomic weights adopted in this work, equal volumes of different elementary gases are supposed to contain, for the most part, equal numbers of atoms of their respective elements, so that the atomic weight of each body in the gaseous state is the weight of a volume of the gas equal to that of a quantity of hydrogen whose weight is taken as unity; in other words, the atomic weights of the simple gases are expressed by the same numbers as their specific gravities referred to hydrogen as unity. This is sometimes expressed by saying that an atom of each elementary gas occupies *one* volume. The only exceptions to this law are presented by phosphorus and arsenic, whose densities in the gaseous state are double of what they should be if they followed the law; and by selenium and tellurium, whose vapour-densities have not yet been ascertained with certainty. Sulphur-vapour was formerly supposed to have a density three times as great as that which the general law just stated requires, but recent experiments have shown that it conforms to the general law.

The atoms or molecules of compound bodies in the gaseous state occupy, for the most part, *twice* the volume of an atom of hydrogen or other simple gas; in other words, the number of molecules of a compound gas contained in a given space is half the number of atoms of hydrogen which would be included in that same space. Consequently, the specific gravity of a compound gas or vapour referred to hydrogen as unity is equal to half the atomic weight. Thus, the atomic weight of hydrochloric acid (HCl) is 36·5, and its specific gravity referred to hydrogen is 18·25; the atomic weight of ammonia (NH^3) is 17, and its specific gravity referred to hydrogen is 8·5. (For the further development of this law, and for certain exceptions to it, real and apparent, see the article ATOMIC WEIGHTS.)

The mode of stating these laws of gaseous atomic volume, must of course be modified according to the system of atomic weights chosen. On that which has hitherto been most generally adopted ($H = 1$, $O = 8$, $S = 16$, &c.), some of the elementary gases, viz. chlorine, iodine, bromine, nitrogen, and mercury are supposed to have atomic volumes equal to that of hydrogen, while oxygen, sulphur, phosphorus, and arsenic have atomic volumes only half as great. The former are generally called *two-volume* gases, and the latter *one-volume* gases, the volume of oxygen being taken as the unit. On the same system, the molecules of most compound bodies in the gaseous state are said to occupy *four* volumes.

Atomic Volumes of Liquids and Solids.

1. **Of Elementary Bodies.** The following table contains the atomic volumes of those solid and liquid elements whose densities have been determined with accuracy. The numbers in the third column are the quotients of the atomic weights divided by the specific gravities referred to water as unity:

Substance.	Atomic weight.	Atomic volume.	Specific gravity (water = 1).
Aluminium . .	13·75	5·3	2·5—2·67, Wöhler; 2·67, Deville.
Antimony . .	120·3	17·9	6·72, Marchand and Scheerer; Kopp.
Arsenic . . .	75	13·3	5·63, Karsten; 5·67, Herapath.
Bismuth . .	210	21·2	9·80, Marchand and Scheerer; 9·78, Kopp.
Bromine . .	80	25·8	*Liquid:* 3·19, Pierre; 2·99, Löwig.
Cadmium . .	56	6·5	8·69, Stromeyer; 8·45, Kopp.
Calcium . .	20	12·6	1·58, Bunsen.
Carbon . . .	12	3·4	*Diamond:* 3·52, Brisson.
		5·2	*Graphite:* 2·32, Karsten; 2·27, Regnault.
Chlorine . .	35·5	26·7	*Liquid:* 1·33, Faraday.
Chromium . .	26·2	3·8	7·01, Bunsen and Frankland.
Cobalt . . .	29·5	3·5	8·49, Brunner; 8·51, Berzelius.
Copper . . .	31·7	3·6	8·95, Marchand and Scheerer; 8·93, Kopp.
Glucinum . .	4·7	2·2	2·1, Debray.
Gold . . .	196	10·2	19·34, G. Rose; 19·26, Brisson.
Iodine . . .	127	25·7	4·95, Gay-Lussac.
Iridium . . .	99	4·5	21·80, Hare.
Iron . . .	28	3·6	7·84, Broling; 7·79, Karsten
Lead . . .	103·6	9·2	11·39, Karsten; 11·33, Kopp.
Lithium . .	7	11·9	0·59, Bunsen.
Magnesium . .	12	6·9	1·74, Bunsen; 1·70. Kopp.
Manganese . .	27·6	3·5	8·03, Bachmann; 8·01, John.
Mercury . .	100	7·4	*Liquid:* 13·60, Regnault, Kopp.
Molybdenum . .	46	5·3	8·62—8·64, Buchholz.
Nickel . . .	29·5	3·4	8·60, Brunner; 8·82, Tupputi.
Palladium . .	53	4·6	11·80, Wollaston.
Phosphorus . .	31	16·8	*Yellow:* 1·84, Schrötter; 1·83, Kopp.
		15·8	*Red:* 1·96, Schrötter.
Platinum . .	99	4·6	21·5, Wollaston, Berzelius.
Potassium . .	39·2	45·6	0·86, Gay-Lussac and Thenard.
Rhodium . .	52	4·7	11·0, Wollaston; 11·2, Cloud.
Selenium . .	79	18·4	*Amorphous:* 4·28, Schaffgotsch.
		16·4	*Granular:* 4·80, Schaffgotsch.
Silicon . . .	28	11·2	*Graphitoïdal:* 2·49, Wöhler.
Silver . . .	108	10·2	10·4, Karsten, 10·57, G. Rose.
Sodium . . .	23	23·7	0·97, Gay-Lussac and Thenard.
Strontium . .	43·8	17·2	2·54, Bunsen.
Sulphur . .	32	15·2	*Trimetric:* 2·07, Marchand and Scheerer, Kopp.
		16·2	*Monoclinic:* 1·98, Marchand and Scheerer.
Tellurium . .	128	20·6	6·24, Berzelius; 6·18, Löwe.
Tin . . .	118	16·2	7·29, Karsten; 7·30, Kopp.
Tungsten . .	92	5·3	17·2, Allen and Aiken; 17·5—18·3, Wöhler.
Uranium . .	60	3·3	18·4, Péligot.
Zinc . . .	32·5	4·6	7·13, Kopp; 7·1—7·2, Bolley.

The numbers in the third column of this table, do not exhibit the simplicity of relation which exists between the atomic volumes of gaseous bodies. There are, indeed, several causes which interfere with the existence, or at least with the observation, of such simple relations between the atomic volumes of solid and liquid elements. In the first place, the densities of three of them, viz. mercury, bromine, and chlorine, are such as belong to them in the liquid state, whereas the densities assigned to all the others have been determined in the solid state. In solids, moreover, the density is greatly affected by the state of aggregation, whether crystalline or amorphous, and in dimorphous bodies, each form has a density peculiar to itself. Further, as solids and liquids are variously affected by heat, each having a peculiar rate of expansion, and that rate being different at different temperatures, it is not to be expected that their atomic volumes should exhibit simple relations, unless they are compared at temperatures at which they are similarly affected by heat. Even gases are found to exhibit abnormal atomic volumes if compared at temperatures too near the points at which they pass into the liquid state. In liquids, the simplest relations of atomic volume are found at those temperatures for which the tensions of the vapours are equal (Kopp); and in solids, the melting points are most probably the comparable temperatures. Now the specific gravities of most of the solid elements in the preceding table, have been determined at mean temperatures (as at 15°·5 C.), which, in the case of potassium, sodium, phosphorus, and a few others, do not differ greatly from the melting points, but in other cases, as with gold, platinum, iron, &c., are removed from the melting points by very long intervals. In spite, however, of these causes of divergence, the atomic volumes of certain analogous elements are very nearly equal to each other: viz. those of selenium and sulphur; of chromium, iron, cobalt, copper, manganese and nickel; of molybdenum and tungsten; of iridium, platinum, palladium and rhodium; and of gold and silver.

2. **Of Liquid Compounds.** The relations between the atomic volumes of liquids, have been investigated chiefly by H. Kopp (Ann. Ch. Pharm. xcvi. 153, 303, c. 19). The atomic volumes of liquids, as already observed, are comparable only at temperatures for which the tensions of their vapours are equal, as at the boiling points. If the atomic weights are compared with the densities at equal temperatures, no regular relations can be perceived; but when the same comparison is made at the boiling points of the respective liquids, several remarkable laws become apparent. The density of a liquid at its boiling point cannot be ascertained by direct experiment; but when the density at any one point, say at 15·5° C., has been ascertained, and the rate of expansion is also known, the density at the boiling point may be calculated. (See EXPANSION.)

Table A. contains Kopp's determinations of the atomic volumes of several liquids containing carbon, hydrogen, and oxygen, at their boiling points. The atomic weights are those of the hydrogen scale. The *calculated* atomic volumes in the fourth column are determined by a method to be presently described; the *observed* atomic volumes are the quotients of the atomic weights divided by the specific gravities at the boiling referred to water as unity.

TABLE A.

Atomic Volumes of Liquids containing Carbon, Hydrogen, and Oxygen.

	Substance.	Formula.	Atomic Weight.	Atomic Volume at the Boiling Point.	
				Calculated.	Observed.
Type HH.	Benzene	C^6H^6	78	99·0	96·0... 99·7 at 80° C.
	Cymene	$C^{10}H^{14}$	134	187·0	183·5...185·2 „ 175
	Naphthalin . . .	$C^{10}H^8$	128	154·0	149·2 . . „ 218
	Aldehyde	C^2H^4O	44	56·2	56·0... 56·9 „ 21
	Valeraldehyde . .	$C^5H^{10}O$	86	122·2	117·3...120·3 „ 101
	Bitter almond oil . .	C^7H^6O	106	122·2	118·4 . . „ 179
	Cuminol . . .	$C^{10}H^{12}O$	148	188·2	189·2 . . „ 236
	Tetryl	C^8H^{18}	114	187·0	184·5...186·8 „ 108
	Acetone	C^3H^6O	58	78·2	77·3... 77·6 „ 56
Type HH.O.	Water	H^2O	18	18·8	18·8 . . „ 100
	Wood-spirit . . .	CH^4O	32	40·8	41·9... 42·2 „ 59
	Alcohol	C^2H^6O	46	62·8	61·8... 62·5 „ 78
	Amylic alcohol . .	$C^5H^{12}O$	88	128·8	123·6...124·4 „ 135
	Phenylic alcohol . .	C^6H^6O	94	106·8	103·6...104·0 „ 194
	Benzylic alcohol . .	C^7H^8O	108	128·8	123·7 . . „ 213
	Formic acid . . .	CH^2O^2	46	42·0	40·9... 41·8 „ 99
	Acetic acid . . .	$C^2H^4O^2$	60	64·0	63·5... 63·8 „ 118
	Propionic acid . .	$C^3H^6O^2$	74	86·0	85·4 . . „ 137
	Butyric acid . . .	$C^4H^8O^2$	88	108·0	106·4...107·8 „ 156
	Valerianic acid . .	$C^5H^{10}O^2$	102	130·0	130·2...131·2 „ 175
	Benzoic acid . . .	$C^7H^6O^2$	122	130·0	126·9 . . „ 253

TABLE A (*continued*).

	Substance.	Formula.	Atomic Weight.	Atomic Volume at the Boiling Point.	
				Calculated.	Observed.
Type HH.O.	Ethylic ether	$C^4H^{10}O$	74	106·8	105·6...106·4 at 34 °C.
	Acetic anhydride	$C^4H^6O^3$	102	109·2	109·9...110·1 „ 138
	Formate of methyl	$C^2H^4O^2$	60	64·0	63·4 . . „ 36
	Acetate of methyl	$C^3H^6O^2$	74	86·0	83·7... 85·8 „ 55
	Formate of ethyl	$C^3H^6O^2$	74	86·0	84·9... 85·7 „ 55
	Acetate of ethyl	$C^4H^8O^2$	88	108·0	107·4...107·8 „ 74
	Butyrate of methyl	$C^5H^{10}O^2$	102	130·0	125·7...127·3 „ 93
	Propionate of ethyl	$C^5H^{10}O^2$	102	130·0	125·8 . . „ 93
	Valerate of methyl	$C^6H^{12}O^2$	116	152·0	148·7...149·6 „ 112
	Butyrate of ethyl	$C^6H^{12}O^2$	116	152·0	149·1...149·4 „ 112
	Acetate of tetryl	$C^6H^{12}O^2$	116	152·0	149·3 . . „ 112
	Formate of amyl	$C^6H^{12}O^2$	116	152·0	149·4...150·2 „ 112
	Valerate of ethyl	$C^7H^{14}O^2$	130	174·0	173·5...173·6 „ 131
	Acetate of amyl	$C^7H^{14}O^2$	130	174·0	173·3...175·5 „ 131
	Valerate of amyl	$C^{10}H^{20}O^2$	172	240·0	244·1 . . „ 188
	Benzoate of methyl	$C^8H^8O^2$	136	152·0	148·5...150·3 „ 190
	Benzoate of ethyl	$C^9H^{10}O^2$	150	174·0	172·4...174·8 „ 209
	Benzoate of amyl	$C^{12}H^{16}O^2$	192	240·0	247·7 . . „ 266
	Cinnamate of ethyl	$C^{11}H^{12}O^2$	176	207·0	211·3 . . „ 260
Type 2(HH.O).	Acid salicylate of methyl	$C^8H^8O^3$	152	159·8	156·2...157·0 „ 223
	Carbonate of ethyl	$C^5H^{10}O^3$	118	137·8	138·8...139·4 „ 126
	Oxalate of methyl	$C^4H^6O^4$	118	117·0	116·3 . . „ 162
	Oxalate of ethyl	$C^6H^{10}O^4$	146	161·0	166·8...167·1 „ 186
	Succinate of ethyl	$C^8H^{14}O^4$	174	205·0	209·0 . . „ 217

A comparison of the numbers in this table, leads to the following results: —

1. *Differences of atomic volume are in numerous instances proportional to the differences between the corresponding chemical formulæ.* — Thus, liquids whose formulæ differ by $n . CH^2$, differ in atomic volume by $n . 22$; for example, the atomic volumes of formate of methyl, $C^2H^4O^2$, and butyrate of ethyl, $C^6H^{12}O^2$, differ by nearly $4 . 22$. Acetate of ethyl, $C^4H^8O^2$, and butyrate of methyl, $C^5H^{10}O^2$. whose formulæ differ by CH^2, differ in atomic volume by nearly 22. The same law holds good with respect to liquids containing sulphur, chlorine, iodine, bromine, and nitrogen (see Tables B, C, D). Again, by comparing the atomic volumes of analogous chlorine and bromine compounds, it is found that the substitution of 1, 2, or 3 atoms of bromine for an equivalent quantity of chlorine, increases the atomic volume of a compound by once, twice, or three times 5. This will be seen by comparing the atomic volumes of PBr^3 and PCl^3; C^2H^5Br and C^2H^5Cl, &c. (Table C.)

2. *Isomeric liquids belonging to the same chemical type have equal atomic volumes.* — The atomic volume of acetic acid, $\left.\begin{matrix}C^2H^3O\\H\end{matrix}\right\}O$ is between 63·5 and 63·8; that of formate of methyl, $\left.\begin{matrix}CHO\\CH^3\end{matrix}\right\}O$ is 63·4; the atomic volume of butyric acid, $\left.\begin{matrix}C^4H^7O\\H\end{matrix}\right\}O$ is between 106·4 and 107·8; that of acetate of ethyl, $\left.\begin{matrix}C^2H^3O\\C^2H^5\end{matrix}\right\}O$ is between 107·4 and 107·8.

3. *In liquids of the same chemical type, the replacement of hydrogen by an equivalent quantity of oxygen* (that is to say, of 1 pt. of hydrogen by 8 pts of oxygen), *makes but a slight alteration in the atomic volume.*—This may be seen by comparing the atomic volumes of alcohol, C^2H^6O, and acetic acid, $C^2H^4O^2$; of ether, $C^4H^{10}O$, acetate of ethyl, $C^4H^8O^2$, and anhydrous acetic acid, $C^4H^6O^3$; of cymene, $C^{10}H^{14}$, and cuminol, $C^{10}H^{12}O$. The alteration caused by the substitution of O for H^2 is always an increase.

4. *In liquids of the same chemical type, the replacement of 2 at.* H *by 1 at* C (1 pt. by weight of hydrogen by 6 parts of carbon) *makes no alteration in the atomic volume.* —Such, for example, is the case with benzoate of ethyl, $C^9H^{10}O^2$, and valerate of ethyl, $C^7H^{14}O^2$, and with the corresponding benzoates and valerates in general; also

with bitter-almond oil, C^7H^6O, and valeraldehyde, $C^5H^{10}O$; also with phenylic alcohol, C^6H^6O, and vinic ether, $C^4H^{10}O$.

In liquids belonging to different types, the same relations are not found to hold good. Moreover, the types within which these relations are observed, are precisely those of Gerhardt's classification (see CLASSIFICATION). Further, when liquid compounds are represented by rational formulæ founded on these types, their atomic volumes may be calculated from certain fundamental values of the atomic volumes of the elements, on the supposition that the atomic volume of a liquid compound is equal to the sum of the atomic volumes of its constituent elements. In this manner the calculated atomic volumes in the fourth columns of tables A, B, C, D are determined. It must be understood however that these values are based upon somewhat doubtful assumptions respecting the atomic volumes of the elements, and are regarded by Kopp merely as approximations to the truth.

Since the addition of CH^2 to a compound increases the atomic volume by 22, this number may be taken to represent the atomic volume of CH^2; moreover, since C may take the place of H^2 in combination, without altering the atomic volume of the compound, it follows that the atomic volume of C must be equal to that of H^2; and therefore the atomic volume of C $= \frac{22}{2} = 11$, and that of H^2 also equal to 11, or that of H = 5·5. Further, as the substitution of O for H^2 produces a slight increase in the atomic volume of a compound, the atomic volume of O must be rather greater than 11; and it is found that, by assuming the atomic volume of O, when it takes place of H^2 (that is to say, in a radicle, as when acetyl, C^2H^3O, is formed from ethyl, C^2H^5), to be equal to 12·2, results are obtained agreeing very nearly with those of observation. But when oxygen occupies the position which it has in water, $\frac{H}{H}O$, its atomic volume is smaller. The specific gravity of water at the boiling point is 0·9579; hence its atomic volume at that temperature is $\frac{18}{0 \cdot 9579} = 18 \cdot 8$; now the 2 atoms of hydrogen occupy a space equal to 11; hence the volume of the oxygen is 7·8. The same value of the atomic volume substituted for O in the formula of the several compounds belonging to the water-type, in which it occupies a similar place, that is to say, outside the radicle, gives results agreeing nearly with observation. That a given quantity of a substance should occupy different spaces, under different circumstances, is a fact easily explained, when it is remembered that the particles of a body cannot be supposed to be in absolute contact, but are separated by certain spaces, which, increase or diminish according to the temperature of the body, and according as it is in the solid, liquid, or gaseous state.

From these values of the atomic volumes of the elements, carbon, hydrogen, and oxygen; viz.

Atomic volume of C . . . . = 11
" " H . . . . = 5·5
" " O (within the radicle) . . . . . = 12·2
" " O (without the radicle) . . . . . = 7·8

the calculated values of the atomic volumes of liquids, in the fourth column of Table A are deduced. The method of calculation may be understood from the following examples:

Benzene, $C^6H^6 = C^6H^5.H$.

Atomic volume of C^6 . . . . = 66
" " H^6 . . . . = 33
" " benzene . . . . = 99

Aldehyde, $C^2H^4O = C^2H^3O.H$.

Atomic volume of C^2 . . . . = 22
" " H^4 . . . . = 22
" " O (within the radicle) . . . . = 12·2
" " aldehyde . . . . = 56·2

Alcohol, $C^2H^6O = \left.\begin{matrix}C^2H^5\\H\end{matrix}\right\}O$.

Atomic volume of C^2 . . . . = 22
" " H^6 . . . . = 33
" " O (without the radicle) . . . . = 7·8
" " alcohol . . . . = 62·8

Acetic acid, $C^2H^4O^2 = \left.\begin{matrix} H \\ C^2H^3O \end{matrix}\right\} O.$

Atomic volume of C^2 . . . . = 22
„ „ H^4 . . . . = 22
„ „ O (within the radicle) . . . = 12·2
„ „ O (without the radicle) . . . = 7·8
„ „ acetic acid . . . . . . = 64·0

Acetic anhydride $C^4H^6O^3 = \left.\begin{matrix} C^2H^3O \\ C^2H^3O \end{matrix}\right\} O.$

Atomic volume of C^4 . . . . = 44
„ „ H^6 . . . . = 33
„ „ O^2 (within the radicle) . . . = 24·4
„ „ O (without the radicle) . . . = 7·8
„ „ acetic anhydride . . . . . . = 109·2

Oxalate of methyl, $C^4H^6O^4 = \left.\begin{matrix} C^2O^2 \\ (CH^3)^2 \end{matrix}\right\} O^2.$

Atomic volume of C^4 . . . . = 44
„ „ H^6 . . . . = 33
„ „ O^2 (within the radicle) . . . = 24·4
„ „ O^2 (without the (radicle) . . . = 15·0
„ „ oxalate of methyl . . . . . . = 117·0

Liquids containing Sulphur.—Sulphur enters into combination in various ways; sometimes taking the place of oxygen in the type HH.O (as in mercaptan); sometimes taking the place of carbon within a radicle (as in sulphurous anhydride) SO.O, compared with carbonic anhydride CO.O; sometimes replacing oxygen within a radicle (as in sulphide of carbon), CS.S, compared with carbonic anhydride. In the first and second cases, the atomic volume of sulphur-compounds may be calculated by attributing to sulphur, (S = 32), the atomic volume 22·6, those of the other elements remaining as above; in the third case, the atomic volume of sulphur appears to be greater; viz. 28·6.

Ex.—*Mercaptan,* $C^2H^6S = \left.\begin{matrix} C^2H^5 \\ H \end{matrix}\right\} S.$

Atomic volume of C^2 . . = 22
„ „ H^6 . . = 33
„ „ S . . = 22·6
„ „ mercaptan . = 77·6

Sulphide of carbon, CS^2 = CS.S.

Atomic volume of C . . = 11
„ „ S (within the radicle) . = 28·6
„ „ S (without the radicle) . = 22·6
„ sulphide of carbon . = 62·2

TABLE B.—*Atomic Volumes of Liquid Sulphur-compounds.*

Substance.	Formula.	Atomic Weight.	Atomic Volume at the Boiling Point.	
			Calculated.	Observed.
Mercaptan . . .	C^2H^6S	62	77·6	76·0... 76·1 at 36° C.
Amylic mercaptan . .	$C^5H^{12}S$	104	143·6	140·1...140·5 „ 120
Sulphide of methyl .	C^2H^6S	62	77·6	75·7 . . „ 41
Sulphide of ethyl . .	$C^4H^{10}S$	90	121·6	120·5...121·5 „ 91
Disulphide of methyl .	$C^2H^6S^2$	94	100·2	100·6...100·7 „ 114
Sulphurous anhydride .	SO^2	64	42·6	43·9 . . „ —8
Sulphite of ethyl . .	$C^4H^{10}SO^3$	138	149·4	148·8...149·5 „ 160
Sulphide of carbon .	CS^2	76	62·2	62·2... 62·4 „ 47

Chlorides, Bromides, and Iodides.—In liquid compounds of this class, the atomic volume of Cl is supposed to be 22·8, that of Br = 27·8, and that of I = 37·5, those of the other elements remaining as above.

Table C.—*Atomic Volumes of Liquid Chlorides, Bromides, and Iodides.*

Substance.	Formula.	Atomic Weight.	Atomic Volume at the Boiling Point.	
			Calculated.	Observed.
Dichlorinated ethylene .	$C^2H^2Cl^2$	97	78·6	73·9 . at 37° C.
Chloride of carbon . .	C^2Cl^4	166	113·2	115·4 . . ,, 123
Chloride of ethylene . .	$C^2H^4Cl^2$	99	89·6	85·8... 86·4 ,, 85
,, monochlorinated .	$C^2H^3Cl^3$	133·5	106·9	105·4...107·2 ,, 115
,, dichlorinated .	$C^2H^2Cl^4$	168	124·2	120·7...121·4 ,, 137
,, trichlorinated .	C^2HCl^5	202·5	141·5	143 . . ,, 154
Chloride of tetrylene .	$C^4H^8Cl^2$	127	133·6	129·5...133·7 ,, 123
Monochlorinated chloride of methyl . . .	CH^2Cl^2	85	67·6	64·5 . . ,, 30·5
Chloroform . . .	$CHCl^3$	119·5	84·9	84·8... 85·7 ,, 62
Chloride of carbon . .	CCl^4	154	102·2	104·3...107·0 ,, 78
Chloride of ethyl . .	C^2H^5Cl	64·5	72·3	71·2... 74·5 ,, 11
,, monochlorinated .	$C^2H^4Cl^2$	99	89·6	86·9... 89·9 ,, 64
,, dichlorinated .	$C^2H^3Cl^3$	133·5	106·9	105·6...109·7 ,, 75
Chloride of amyl . .	$C^5H^{11}Cl$	106·5	138·3	135·4...137·0 ,, 102
Chloral	C^2HCl^3O	147·5	108·1	108·4...108·9 ,, 96
Chloride of acetyl . .	C^2H^3OCl	78·5	73·5	74·4... 75·2 ,, 55
Chloride of benzoyl . .	C^7H^5OCl	140·5	139·5	134·2...137·8 ,, 198
Bromine	Br^2	160	55·6	54 ... 28·7 ,, 63
Bromide of methyl . .	CH^3Br	95	55·3	58·2 . . ,, 13
Bromide of ethyl . .	C^2H^5Br	109	77·3	78·4 . . ,, 41
Bromide of amyl . .	$C^5H^{11}Br$	151	143·3	149·2 . . ,, 119
Bromide of ethylene . .	$C^2H^4Br^2$	188	99·6	97·5... 99·9 ,, 130
Iodide of methyl . .	CH^3I	142·1	65·0	65·4... 68·3 ,, 43
Iodide of ethyl . .	C^2H^5I	156·1	87·0	85·9... 86·4 ,, 71
Iodide of amyl . .	$C^5H^{11}I$	198·1	153·0	152·5...155·8 ,, 147
Chloride of sulphur . .	SCl	67·5	. .	45·7 . . ,, 140
Chloride of phosphorus .	PCl^3	137·5	. .	93·9 . . ,, 78
Bromide of phosphorus .	PBr^3	271	. .	108·6 . . ,, 175
Chloride of silicon . .	$SiCl^4$	170	. .	121·6 . . ,, 59
Bromide of silicon . .	$SiBr^4$	348	. .	144·0 . . ,, 153
Chloride of arsenic . .	$AsCl^3$	181·5	. .	94·8 . . ,, 133
Chloride of antimony .	$SbCl^3$	235·5	. .	100·7 . . ,, 223
Bromide of antimony .	$SbBr^3$	369	. .	116·8 . . ,, 275
Chloride of tin . .	$SnCl^4$	260	. .	132·4 . . ,, 115
Chloride of titanium . .	$TiCl^4$	92	. .	126·0 . . ,, 136

The compounds PCl^3 and $AsCl^3$, have nearly equal atomic volumes: whence it may be inferred that phosphorus, and arsenic, in their liquid compounds, have equal atomic volumes. The same conclusion may be drawn regarding tin and titanium since the atomic volumes of $SnCl^4$ and $TiCl^4$ are nearly equal.

Nitrogen-compounds.—In compounds belonging to the ammonia type, the atomic volume of nitrogen is 2·3. This result is deduced from the observed atomic volume of phenylamine C^6H^7N, which is 106·8. Now the atomic volume of $6C + 7H = 6 . 11 + 7 . 5·5 = 104·5$, which number, deducted from 106·8, leaves 2·3 for the atomic volume of nitrogen.

The atomic volume of cyanogen deduced from the observed atomic volume of cyanide of phenyl, $CN.C^6H^5$, or C^7H^5N, is nearly 28. Thus:—

$$\begin{array}{lllr} \text{Atomic volume of} & C^7H^5N & = & 121·6 \\ ,, \quad\quad ,, & C^6H^5 & = & \underline{93·5} \\ ,, \quad\quad ,, & CN & = & 28·1 \end{array}$$

A similar calculation, founded on the observed atomic volume of cyanide of methyl, C^2H^3N, gives, for the atomic volume of cyanogen, the number 26·8. The atomic volume of liquid cyanogen determined directly at 37° or 39° C. above its boiling point, is between 28·9 and 30·0. As a mean of these values, the atomic volume of cyanogen may be assumed to be 28; and with this value the atomic volumes of the liquid cyanides are calculated. Thus, for

Oil of mustard (sulphocyanate of allyl), $C^4H^5NS = \left.\begin{matrix}CN\\C^3H^5\end{matrix}\right\}S$.

Atomic volume of C^3H^5 . . . . = 60·5
" " CN . . . . = 28·0
" " S (without the radicle) = 22·6
" " oil of mustard . . = 111·1

The atomic volumes of compounds containing the radicle NO^2, are calculated on the hypothesis that the atomic volume of that radicle is 33, which agrees nearly with the observed atomic volume of liquid peroxide of nitrogen. Thus: the atomic volume of nitrite of amyl, $C^5H^{11}NO^2$ = at. vol. of C^5H^{11} + at. vol. of $NO^2 = 115·5 + 33 = 148·5$.

TABLE D.—*Atomic Volumes of Liquids containing Nitrogen.*

Substance.	Formula.	Atomic Weight.	Atomic Volume at the Boiling Point.	
			Calculated.	Observed.
Ammonia . . .	H^3N	17	18·8	22·4... 23·3 at 10°...16° C.*
Ethylamine . .	C^2H^7N	45	62·8	65·3 . . at 18·7
Tetrylamine . .	$C^4H^{11}N$	73	106·8	
Amylamine . . .	$C^5H^{13}N$	87	128·8	125·0 . . " 94
Octylamine . . .	$C^8H^{19}N$	129	194·8	190·0 . . " 170
Phenylamine . .	C^6H^7N	93	106·8	106·4...106·8 . " 184
Toluidine . . .	C^7H^9N	107	128·8	
Ethylphenylamine .	$C^8H^{11}N$	121	150·8	150·6 . . " 204
Diethylphenylamine .	$C^{10}H^{15}N$	149	194·8	190·5 . . " 213·5
Cyanogen . . .	CN	26	28·0	28·9... 30·0 . " 16 †
Hydrocyanic acid .	CHN	27	33·5	39·1 . . " 27
Cyanide of methyl .	C^2H^3N	41	55·5	54·3 . . " 74
Cyanide of ethyl . .	C^3H^5N	55	77·5	77·2 . . " 88
Cyanide of tetryl .	C^5H^9N	83	121·5	
Cyanide of phenyl .	C^7H^5N	103	121·5	121·6...121·9 . " 191
Sulphocyanate of methyl	C^2H^3NS	73	78·1	75·2... 78·2 . " 133
Sulphocyanate of ethyl	C^3H^5NS	87	100·1	99·1 . . " 146
Oil of mustard . .	C^4H^5NS	99	111·1	113·1...114·2 . " 148
Cyanate of ethyl . .	C^3H^5NO	71	85·3	84·3... 84·8 . " 60
Peroxide of nitrogen .	NO^2	30	33·0	31·7... 32·4 . " 40 ‡
Nitrate of methyl .	CH^3NO^3	77	68·3	69·4 . . " 66
Nitrate of ethyl . .	$C^2H^5NO^3$	101	90·3	90·0... 90·1 . " 86
Nitrobenzene . .	$C^6H^5NO^2$	123	126·5	122·6...124·9 . " 218
Nitrite of methyl . .	$CH NO^2$	161	60·5	61·6 . . " 14 §
Nitrite of ethyl . .	$C^2H^5NO^2$	75	82·5	79·2... 84·6 . " 18
Nitrite of amyl . .	$C^5H^{11}NO^2$	117	148·5	148·4 . . " 95

From the preceding observations and calculations, it appears that the atomic volume of a compound depends, not merely on its empirical, but likewise on its rational formula; in other words, not merely on the number of atoms of its elements, but further on the manner in which those atoms are arranged. Now a compound may have more than one rational formula, according to the manner in which it decomposes; and hence it might appear that the calculation of atomic volumes must be attended with considerable uncertainty, inasmuch as the atomic volumes of certain elements, as oxygen and sulphur, vary according to the manner in which they enter into the compound. Aldehyde, for example, may be represented either as $\left.\begin{matrix}C^2H^3\\H\end{matrix}\right\}O$, or as $\left.\begin{matrix}C^2H^3O\\H\end{matrix}\right\}$; and, as the atomic volume of oxygen is 12·2 or 7·8, according as it is within or without the radicle, the atomic volume of aldehyde will be 56·2 if deduced from the type HH, and

---

* Between 44° and 50° above the boiling point.

† Between 37° and 39° above the boiling point.

‡ About 55° above the boiling point.

§ 27° above the boiling point.

51·8 if deduced from the type HH.O. But the atomic weight of aldehyde, and its specific gravity at a given temperature are invariable; it cannot therefore have two different atomic volumes. It must be remembered, however, that, in speaking of a compound as having several rational formulæ, we consider it rather in a dynamical than in a statical point of view; as under the influence of disturbing forces, and on the point of undergoing chemical change. But if, on the other hand, we regard a compound in its fixed statical condition, as a body possessing definite physical properties, a certain specific gravity, a certain boiling point, rate of expansion, refractive power, &c., we can scarcely avoid attributing to it a fixed molecular arrangement, or, at all events, supposing that the disposition of its atoms is confined within those limits which constitute chemical types. It is found, indeed, that isomeric liquids exhibit equal atomic volumes only when they belong to the same chemical type. If this view be correct, the relation between the atomic volumes of elements and compounds, may often render valuable service in determining the rational formula which belongs to a compound in the state of rest. Thus of the two atomic volumes just calculated for aldehyde, the number 56·2, deduced from the formula $C^2H^3O.H$, agrees with the observed atomic volume of aldehyde, which is between 56·0 and 56·9, better than 51·8, the number deduced from  $\left.\begin{matrix}C^2H^3\\H\end{matrix}\right\}O$. This result leads to the conclusion that the aldehydes belong to the hydrogen type rather than to the water type.

There are many groups of liquid compounds, irrespective of isomerism or similarity of type, the members of which have equal or nearly equal atomic volumes. The following table exhibits the calculated atomic volumes of several of these groups:

Water . . .	H^2O	18·8	Ether . . .	$C^4H^{10}O$	106·8
Ammonia . . .	NH^3	18·8	Tetrylic alcohol .	$C^4H^{10}O$	106·8
			Phenylic alcohol .	C^6H^6O	106·8
Bromine . . .	Br^2	55·6	Tetrylamine . .	$C^4H^{11}N$	106·8
Cyanogen . . .	$(CN)^2$	56·0	Phenylamine . .	C^6H^7N	106·8
Aldehyde . . .	C^2H^4O	56·2	Butyric acid . .	$C^4H^8O^2$	108·0
Cyanide of methyl .	C^2H^3N	55·5	Acetate of ethyl .	$C^4H^8O^2$	108·0
Bromide of methyl .	CH^3Br	55·3	Acetic anhydride .	$C^4H^6O^3$	109·2
			Chloral . . .	C^2HCl^3O	108·1
Alcohol . . .	C^2H^6O	62·8	Dichlorinated chloride of ethyl . .	$C^2H^3Cl^3$	106·9
Acetic acid . .	$C^2H^4O^2$	64·0			
Formate of methyl .	$C^2H^4O^2$	64·0	Monochlorinated chloride of ethylene .	$C^2H^3Cl^3$	106·9
Cyanate of methyl .	C^2H^3NO	63·3			
Ethylamine . .	C^2H^7N	62·8	Bromide of phosphorus . . .	PBr^3	108·6
Sulphide of carbon .	CS^2	62·3			
Iodide of methyl .	CH^3I	65·0			
			Valeraldehyde . .	$C^5H^{10}O$	122·2
Acetone . . .	C^3H^6O	78·2	Cyanide of tetryl .	C^5H^9N	121·5
Cyanide of ethyl .	C^3H^5N	77·5	Bitter almond oil .	C^7H^6O	122·2
Sulphocyanate of methyl . . .	C^2H^3NS	78·1	Cyanide of phenyl .	C^7H^5N	121·5
Sulphide of methyl .	C^2H^6S	77·6	Sulphide of ethyl .	$C^4H^{10}S$	121·6

These groups exhibit an approach to the uniformity of atomic volume which is observed in the gaseous state.

Berthelot has adduced a number of examples, showing that when a liquid compound is formed by the union of two other liquids, whose specific volumes are denoted by A and B, with elimination of x atoms of water, the specific volume of the compound is nearly $= A + B - xC$ (the atomic volume of water being denoted by C). Berthelot's observations, however, were made at medium temperatures, not at the boiling points of the liquids (Ann. Ch. Phys. [3] xlviii. 322).

3. **Of Solid Compounds.** (H. Kopp, Pogg. Ann. xlvii. 133; lii. 243, 262; Ann. Ch. Pharm. xxxvi. 1.—Ammermüller, Pogg. Ann. xlix. 341.—H. Schröder, *ibid.* i. 552; lii. 269, 282; cvi. 226; cvii. 113.—Filhol, Ann. Ch. Phys. xxi. 415.—Playfair and Joule, Chem. Soc. Mem. ii. 477; iii. 54, 199; Chem. Soc. Qu. J. i. 121.—H. Schiff, Ann. Ch. Pharm. cvii. 64; cxii. 88.—Gm. i. 67—86.)

The most general relation that has been observed between the atomic volumes of of solid compounds is, that *isomorphous compounds have equal atomic volumes*, in other words, their densities are proportional to their atomic weights. Such is the case, for example, with carbonate of strontium (strontianite) and carbonate of lead (witherite).

Formula.	At. Weight.	Sp. Gr.	At. Volume.
Sr^2CO^3	147·6	3·60	41·0
Pb^2CO^3	267·4	6·47	41·4

If the crystalline forms are only approximately similar, the atomic volumes also are only approximately equal, the difference being less as the angles of the two crystalline forms are more nearly equal, and their axes more nearly in the same ratio. An alteration of atomic volume, such as is often produced by the introduction of one element into a compound in place of another, is attended with a corresponding alteration of crystalline form. The atomic volume may likewise be altered without any change in the composition of the body, viz. by change of temperature, and this also produces in most cases, as Mitscherlich has shown, a corresponding alteration in the magnitude of the angles. In crystals of the regular system, however, variation of temperature produces no alteration either in form or in atomic volume.

In dimorphous compounds, each modification has a density, and therefore also an atomic volume, peculiar to itself.

The equality, exact or approximate, of the atomic volumes of isomorphous compounds, has been traced by Hugo Schiff, through several classes of salts, especially in the sulphates of the general form, $M^2SO^4.7H^2O$ (*vitriols*), in the double sulphates of the magnesian class, $\left.\begin{matrix}K;\ NH^4\\ M\end{matrix}\right\}SO^4.3H^2O$, and in the alums. The atomic volumes of these compounds are given in the following table:

Formula.	Atomic Weight.	Specific Gravity.	Atomic Volume.
Vitriols.			
$Mg^2SO^4 . 7H^2O$	246	1·685	146
$Zn^2SO^4 . 7H^2O$	287	1·853	146·9
$Ni^2SO^4 . 7H^2O$	281·2	1·931	145·6
$Co^2SO^4 . 7H^2O$	281	1·924	146
$Fe^2SO^4 . 7H^2O$	278	1·884	147·5
$(MgCu)SO^4 . 7H^2O$	265·7	1·813	146·5
$MgZnSO^4 . 7H^2O$	266·5	1·817	146·6
$MgCdSO^4 . 7H^2O$	290·0	1·983	146·2
Double Magnesian Sulphates.			
$(NH^4)MgSO^4 . 3H^2O$	180	1·680	107·1
$KMgSO^4 . 3H^2O$	201·2	1·995	100·9
$(NH^4)ZnSO^4 . 3H^2O$	200·5	1·910	104·9
$KZnSO^4 . 3H^2O$	221·7	2·153	103
$(NH^4)NiSO^4 . 3H^2O$	197·6	1·915	103·2
$KNiSO^4 . 3H^2O$	218·8	2·123	103·1
$(NH^4)CoSO^4 . 3H^2O$	197·5	1·873	105·4
$KCoSO^4 . 3H^2O$	218·7	2·154	101·6
$(NH^4)FeSO^4 . 3H^2O$	196	1·813	108·1
$KFeSO^4 . 3H^2O$	217·2	2·189	99·2
$(NH^4)CdSO^4 . 3H^2O$	223·7	2·073	107·9
$KCdSO^4 . 3H^2O$	244·9	2·438	100·5
$(NH)^4CuSO^4 . 3H^2O$	199·7	1·931	103·4
$KCuSO^4 . 3H^2O$	220·9	2·137	103·3
Alums.			
$KAl^2S^2O^8 . 12H^2O$	474·6	1·722	275·6
$NaAl^2S^2O^8 . 12H^2O$	458·4	1·641	279·2
$(NH^4)Al^2S^2O^8 . 12H^2O$	453·4	1·621	279·6
$KCr^2S^2O^8 . 12H^2O$	500·8	1·845	271·4
$(NH^4)Cr^2S^2O^8 . 12H^2O$	479·6	1·736	276·2
$(NH^4)Fe^2S^2O^8 . 12H^2O$	482·0	1·712	281·4

The atomic volumes of the vitriols are very nearly equal; so likewise are those of the alums. Those of the double magnesian sulphates, $M(K;NH^4)SO^43H^2O$, differ somewhat more, the difference between the greatest and least amounting to 8·9. It is remarkable, however, that the atomic volume of the ammonium- and potassium-salts in each pair differs from the mean value (104) by nearly equal values, the former in excess, the latter in defect; thus, in the first pair we find, $107·1 - 104 = +3·1$; and $100·9 - 104 = -3·1$; and in the second pair: $104·9 - 104 = +0·9$; and $103 - 104 = -1·0$.

The following table contains the atomic volumes of certain chlorides, bromides, and iodides:—

Formula.	Atomic Weight.	Specific Gravity.	Atomic Volume.
Chlorides.			
Chloride of hydrogen	36·5	1·501	24·3
Chloride of lead	139·5	5·78	24·2
Chloride of iron (ferrosum)	63·5	2·528	25·1
Chloride of calcium	55·5	2·205	25·2
Chloride of nickel	65·0	2·56	25·3
Chloride of mercuricum	135·5	5·320	25·5
Chloride of silver	143·5	5·517	26·0
Chloride of cuprosum	98·9	3·70	26·7
Chloride of strontium	79·5	2·96	26·9
Chloride of sodium	58·5	2·148	27·2
Chloride of barium	104·1	3·82	27·2
Bromides.			
Bromide of hydrogen	82·0	2·00	41·0
Bromide of mercurosum	281·0	7·307	38·4
Bromide of sodium	104·0	2·952	35·2
Bromide of barium	149·6	4·23	35·3
Bromide of mercuricum	181·0	5·92	30·6
Bromide of silver	189·0	6·353	29·8
Bromide of lead	185·0	6·63	28·0
Iodides.			
Iodide of hydrogen	128·0	2·25	57·0
Iodide of potassium	166·2	2·85	58·3
Iodide of sodium	150·0	3·45	43·5
Iodide of mercurosum	327·0	7·644	42·8
Iodide of silver	235·0	5·35	43·9
Iodide of barium	195·6	4·917	39·8
Iodide of mercuricum	227·0	5·91	38·4
Iodide of lead	231·0	6·07	38·1

It will be observed that the atomic volumes of the bromides and iodides do not agree among themselves so nearly as those of the chlorides. The atomic volume of a bromide is not, for the most part, the mean between those of the corresponding chloride and iodide, but approaches more nearly to that of the chloride. (Schiff.)

That isomorphous compounds do in many instances occupy equal atomic volumes is sufficiently apparent from the preceding examples. Nevertheless, Schröder concludes, from calculations founded partly on his own determinations of specific gravity, partly on those of other observers, that equality of atomic volume is not necessarily connected with similarity of crystalline form, but is exhibited by heteromorphous elements and compounds quite as often as by those which are isomorphous, if not oftener. (Pogg. Ann. cvi. 226; cvii. 113.)

The connection between the atomic volumes of compounds and of their elements has not been so fully examined in solids as in liquids; nevertheless certain general relations have been shown to exist. The most important of these relations, first pointed out by Schröder, and further established by Kopp, is that *equivalent quantities of different elements, in uniting with the same quantity of a given element (or compound radicle) receive equal increments of volume.* Thus, when 207·4 grammes, or 18·44 cub. cent. of lead (Pb^2), 112 grm. = 13 c.c. cadmium (Cd^2), 63·7 grm. = 7·2 c.c. copper (Cu^2), or 65·2 grm. = 9·2 c.c. zinc (Zn^2), unite with 16 grms. of oxygen (O) to form the compounds Pb^2O, Cd^2O, &c., the increment of volume is found to be in each case nearly 2·6 cubic centimetres. Again, in the oxidation of 112 grm. iron (Fe^4) to ferric oxide, Fe^4O^3, the increment of volume is 8·1 = 3 × 2·7 c.c. The explanation of this law appears to be that certain elements enter into combination with the same atomic volume that they occupy in the separate state. Such, according to Kopp, is the case with the heavy metals: so that, by determining experimentally the atomic volumes of their oxides, chlorides, nitrates, &c., and deducting therefrom the volumes of the metals themselves as given in the table (p. 442), the atomic volumes of O, Cl, NO^3, &c.,

which cannot be observed directly, may be found; thus, a comparison of the oxides above-mentioned shows that the atomic volume of oxygen in these compounds is 2·6.

The metals of the alkalis and earths do not appear to enter into combination with the same volume that they occupy in the free state. Their atomic volumes in combination must, therefore, be calculated by deducting from the observed atomic volumes of their salts, the chlorides for example, the volume of the chlorine as determined from the chlorides of the heavy metals, this determination of course resting on the assumption that the atomic volume of the chlorine in combination is the same in all analogous compounds.

On these principles, Kopp has made the following estimations of the atomic volumes of the alkali-metals, earth-metals, and certain salt-radicles:—

NH^4 in its salts	17·4
K „ „	18·7
Na „ „	10·4
Ba „ „	11·4
Sr „ „	8·6
Ca „ „	4·8
CO^3 in the carbonates of Pb, Cd, Fe, Mn, Ag, Zn, Ba, Ca, K, Mg, Na, Sr	12·1
NO^3 in the nitrates of Pb, Ag, NH^4, Ba, K, Na, Sr	28·6
SO^4 in the sulphates of Cu, Ag, Zn, Ca, Mg, Na	18·9
SO^4 in the sulphates of Pb, Ba, K, Sr	14·9
Cl in the chlorides of Pb, Ag, Ba, Na	15·7
Cl in the chlorides of NH^4, Ca, K, Ccu, Hg, Hhg, Sr	19·6
O in the oxides Pb^2O, Cd^2O, Cu^2O, Hg^2O, Zn^2O, SnO, Sb^2O^3, Fe^4O^3, Co^4O^3, Bi^2O^3, Pb^3O^2	2·6
O in the oxides Ccu^2O, Ag^2O, Hhg^2O, Mo^2O^3	5·2

These values were determined in 1841, and many of them require correction according to the atomic weights and densities since established. According to Schröder (*loc. cit.*), the relations upon which they depend are true only with regard to isomorphous compounds, being regulated by the following general law: "If two elements or groups of elements, *A*, *B*, &c., unite with other elements or groups, *C*, *D*, *E*, &c., forming compounds *AC* and *BC*, *AD* and *BD*, *AE* and *BE*, &c., which belong to the same type, and are isomorphous by pairs, the differences of atomic volume of *AC* and *BC*, *AD* and *BD*, *AE* and *BE*, &c., are always equal; but, if these pairs of compound are not isomorphous, or belong to different types, then the differences of atomic volume are unequal."

Messrs. Playfair and Joule have observed some remarkable relations between the atomic volumes of crystallised salts and that of the water which they contain, viz. 1. In certain highly hydrated salts, viz. the *arsenates and phosphates with* 12 *at. water* and in *carbonate of sodium with* 10 *at. water*, the volume of the entire molecule is the same as that of the water of crystallisation frozen into ice, the particles of the acid and base appearing to be interposed between those of the water without increasing the total bulk. The following table contains the specific gravity of some of these salts, as calculated upon this hypothesis, and as determined by direct experiment:

Salt.	Specific Gravity.	
	Exp.	Calc.
$Na^2CO^3 . 10H^2O$	1·454	1·463
$Na^2HPO^4 . 12H^2O$	1·525	1·527
$Na^3PO^4 . 12H^2O$	1·622	1·622
$Na^2HAsO^4 . 12H^2O$	1·736	1·736
$Na^3AsO^4 . 12H^2O$	1·804	1·534

In *cane-sugar* and *milk-sugar*, the atomic volume is the same as that of the hydrogen and oxygen, supposed to be united as water and frozen. Specific gravity of cane-sugar on this hypothesis = 1·586; by experiment = 1·586; of milk-sugar, by calculation 1·534; by experiment 1·531.

2. In another class of salts, including the *hydrated magnesian sulphates* ($M^2O.SO^3 + 6H^2O$), *normal sulphate of aluminium*, *borax*, *pyrophosphate of sodium*, and the *alums*, the atomic volume is made up of the solid water and of the base (M^2O or M^4O^3); in other words, the volume of the hydrated salt is made up of that of the water of crytallisation frozen into ice, and that of the base as it exists in the free state, or in the anhydrous salt. (For details see the memoirs cited on page 449.)

ATOMIC WEIGHTS. The ultimate constitution of matter, and its finite or infinite divisibility, have been made the subjects of speculation and argument from almost the earliest times. The molecular idea of matter seems to have prevailed in the primitive philosophies of the Hindoos, Phœnicians, and Egyptians, from the last of whom it was probably transmitted to the Greeks. Among them, we find the notion of finite divisibility constituting the basis of the cosmogony of Democritus, who apparently acquired the doctrine directly from Leucippus. Subsequently Epicurus, and the Epicureans generally, extended the atomic hypothesis, which, however, was strongly opposed by Empedocles and the later Pythagoreans, who contended for the infinite divisibility of matter, and for its continuity in any given mass. Plato and Aristotle also, especially the latter, advocated the notion of infinite divisibility. In modern times, the doctrine of material atoms was maintained by Newton, and opposed by Descartes, Leibnitz, and Euler. After the time of Euler, the question of the ultimate constitution of matter fell into some neglect, although the non-atomic view seems to have been generally preferred, until Dalton, in 1804—8, revived the atomic hypothesis, in order to account for the phenomena of chemical combination in definite and multiple proportions, which he first brought prominently into notice. Prior to his discovery, the chemical composition of bodies, as determined by analysis, had been expressed in centesimal proportions only, whereby the relations in composition of different bodies were in great measure concealed from observation. Thus, the relative composition of olefiant gas and marsh gas, was expressed very imperfectly by saying that the former contained 85·7 per cent. of carbon and 14·3 per cent. of hydrogen, while the latter contained 75·0 per cent. of carbon and 25·0 per cent. of hydrogen. It was from the results of an examination of these two gases that Dalton was first led to the conception of his theory. He ascertained that both gases consist of carbon and hydrogen only, and set out the centesimal composition of each in the customary manner. But he observed further, that the ratio of hydrogen to carbon is exactly twice as great in the one case as in the other; that in olefiant-gas, for instance, the carbon is to the hydrogen as 6 to 1, whereas in marsh-gas it is as 6 to 2. Or, in other words, a given quantity of carbon unites with either one or two proportions of hydrogen to form the respective compounds, olefiant-gas and marsh-gas. Dalton, whose turn of mind was essentially mechanical, explained the constitution of these two compounds by supposing that the first consisted of 1 at. of carbon united with 1 at. of hydrogen ●⊙, while the second consisted of 1 at. of carbon united with 2 at. of hydrogen ⊙●⊙, the atom of carbon being considered to have 6 times the weight of the atom of hydrogen. He then calculated the composition of other bodies on the same plan, and found, for instance, that the quantity of hydrogen which unites with 6 pts. of carbon to form olefiant gas, unites with 8 pts. of oxygen to form water. Hence water was represented by the symbol ⊙○, the atom of oxygen being considered to have 8 times the weight of the atom of hydrogen. The crowning point of Dalton's theory was reached when he discovered that the numbers which expressed the respective combining proportions of carbon and oxygen with 1 pt. of hydrogen, also expressed the proportions in which they combine with one another. Thus the ratio of carbon to oxygen in carbonic oxide gas was found to be as 6 to 8; whereas in carbonic anhydride gas it was as 6 to *twice* 8. The former compound he considered to result from the union of 1 at. of carbon with 1 at. of oxygen ●○; and the latter to result from the union of 1 at. of carbon with 2 at. of oxygen ○●○. Dalton extended the same views to the compounds of nitrogen, and concluded that the quantity of that element which united with 1 pt. of hydrogen to form ammonia ⦶⊙, united with 8 pts. of oxygen to form nitrous gas ⦶○. We may apply this formula for nitrous gas to the compound known as nitrous anhydride, though, from an error in the rough process of analysis then adopted, it was intended to apply to what is now called nitric oxide, or deutoxide of nitrogen. Even at the present day, it is highly interesting to compare the information afforded by Dalton's expressions for the above-mentioned compounds, with the information afforded by a statement of their respective centesimal proportions, thus:—

	Dalton's Expressions.		Centesimal Proportions.
Olefiant-gas . . .	6 + 1	●⊙	85·72 + 14·28
Marsh-gas . . .	6 + *twice* 1	⊙●⊙	75·00 + 25·00
Water	8 + 1	○⊙	88·89 + 11·11
Carbonic oxide . .	6 + 8	●○	42·86 + 57·14
Carbonic anhydride .	6 + *twice* 8	○●○	27·27 + 72·73
Ammonia . . .	5 + 1	⦶●	82·35 + 17·65
Nitrous gas . . .	5 + 8	⦶○	36·80 + 63·20

Dalton thus established that general principle in chemistry known as the law of combination in definite and multiple proportions. He showed that a particular number might be selected for every element, in such a manner that the proportions by weight in which any two or more elements combine with one another, should be always in the ratios of their respective numbers, or of different multiples of those numbers. And he accounted for this law by supposing that the elements unite with one another atom to atom, and that the proportional number accorded to each particular element expresses the relative weight of its atom. Hydrogen being the lightest substance in nature, was at once chosen by Dalton as the unit in his scale of atomic weights, and the weights of the atoms of other elements were established by ascertaining, directly or indirectly, the respective quantities of those elements which unite either with 1 pt. of hydrogen, or with the quantity of some other element which unites with 1 pt. of hydrogen. But many chemists, who speedily acknowledged the truth of Dalton's laws of combination, refused to admit the atomic doctrine which he had deduced therefrom. Among these was Davy, who introduced the word proportion as a substitute for Dalton's word atom, conceiving the use of the latter word to be objectionable, as involving a theoretical assumption. At the present day, the word atom is most generally employed by chemists; but, while some use it in its strict Daltonian materialistic sense, others use it, in an abstract sense only, to express the smallest indivisible combining proportion of a body, and consider the proportional number of a body as an ultimate or unexplained property pertaining to it. Dalton's symbols were speedily replaced by those now in use, which represent the abbreviated names of the elements. Every such symbol is used to express one atomic proportion of its particular element. Thus, Cl stands for 35·5 pts. of chlorine, Na for 23 pts. of sodium, and As for 75 pts. of arsenic, as compared with 1 pt. by weight of hydrogen. Every compound body being composed of two or more elementary atoms, is expressed by an allocation of symbols. Thus, common salt or chloride of sodium is represented by the formula NaCl, which implies a compound of 23 pts., or 1 combining proportion of sodium, united with 35·5 pts., or 1 combining proportion of chlorine. Again, trichloride of arsenic is represented by the formula $AsCl^3$, which implies a compound of 75 pts., or 1 combining proportion of arsenic, united with 106·5 pts. or 3 combining proportions of chlorine.

The proportional number or atomic weight of a compound body is the sum of the atomic weights of its constituents. Thus, the atomic weight of chloride of sodium is 58·5 and that of trichloride of arsenic 181·5. The relative quantity of a compound body, represented by its formula, is frequently spoken of as its atom, and there is nothing unphilosophical in such an employment of the word. By the atom of sodium, for instance, is understood, the least indivisible proportion of the elementary body sodium, and by the atom of chloride of sodium, the least indivisible proportion of the compound body chloride of sodium, that can have any existence. Soon after the publication of Dalton's theory, it received a valuable corroboration, through its adaptability to groupings of elements or compound atoms. Wollaston, in the course of some analytical experiments, noticed, that if in the two carbonates of potassium, the weight of oxide of potassium be taken as constant, then the weights of carbonic anhydride in each salt are to one another as 1 to 2; and Thomson made a similar observation with regard to the two oxalates of potassium. Hence these salts were represented at that time, in accordance with Dalton's views, as consisting respectively of one compound atom of oxide of potassium, united with one or two compound atoms of carbonic anhydride, and with one or two compound atoms of oxalic anhydride. The compound atom of a body, or more correctly the atom of a compound body, is now often spoken of as its molecule, but in many cases there is a distinction between the application of the two words which will be presently adverted to.

The accuracy of Dalton's laws of combination in definite and multiple proportions, was confirmed by a reference to the previous neglected researches of Wenzel and Richter upon the double decomposition of salts; and by the subsequent brilliant researches of Gay-Lussac upon the laws of combination by volume; in which he showed that the combining proportions of simple and compound gases might be expressed volumetrically or by bulk, as well as numerically or by weight.

It is worth while to refer for a few moments to the above-mentioned experiments of Wenzel and Richter. If we add together solutions of chloride of sodium and nitrate of silver, which are both neutral salts, we get by double decomposition, chloride of silver and nitrate of sodium, and the mixture still remains neutral. There is no redundancy or deficiency of either sodium or silver, but the quantity of sodium separated from its chloride is exactly sufficient to replace the silver separated from its nitrate, and *vice versâ.* Wenzel of Freyberg in Saxony, as early as the year 1777, made very many analyses of salts with great accuracy, and was thereby enabled to account for this neutrality, resulting from the mutual decomposition of neutral salts, by showing that in all salts the quantities of salt-residue, so to speak, which are combined with equal weights of some one metal, will also combine with equal weights of any other metal. Thus, if y grains of chloride of sodium, and z grains of nitrate of sodium alike contain x grains of sodium, then $(y - x) + w$ grains of chloride of silver, and $(z - x) + w$ grains of nitrate of silver will alike contain w grains of silver; because the quantities x and w represent the relative combining proportions of the metals, silver and sodium, which can take the place of one another, and unite with the same amount of chlorine or other salt radicle, or residue. Richter of Breslau in Silesia, published, in the year 1792, what may be regarded as an extension of the views and experiments of Wenzel. He showed that the neutrality of a saline solution does not change during the direct precipitation or substitution of its metal by some other, and that the respective quantities of different metals which displace one another in salts, all unite with the same weight of oxygen. He also constructed a table of the quantities of different oxides or bases, which contain replaceable amounts of metal, and of the quantities of different acids which can be neutralised by those quantities of the respective bases. His experimental results were very inaccurate, but his notions of chemical decomposition, had they received due attention at the time, must have led directly to the doctrine of combining proportions, if not to the Daltonian theory of atoms. It was not until some time after the publication of Dalton's views, that Berzelius first called attention to the prior researches of Wenzel and Richter, as affording a valuable confirmation of the laws of chemical combination which Dalton had enunciated.

In the establishment of proportional numbers or atomic weights, two distinct points have to be considered, namely the exact determination of the ratios, according to which bodies combine, and the correct expression or interpretation of those ratios. The first is a question of experiment, while the second is one of judgment or inference. Thus whether the ratio of hydrogen to nitrogen in ammonia is as 1 to 5, or as 1 to 4·67 is a question of mere experiment: but whether the atom, or smallest indivisible combining proportion of nitrogen is 4·67 times, or 14 times as heavy as the atom or smallest indivisible combining proportion of hydrogen, and consequently, whether the molecule of ammonia consists of one light atom of nitrogen united with 1 of hydrogen, or of one heavy atom of nitrogen united with 3 of hydrogen, are questions for the judgment, which can only be decided by an intimate acquaintance with, and careful consideration of very many circumstances relating to the respective bodies and their congeners. The numbers originally chosen by Dalton to express the ratios in which the different elements unite with 1 part of hydrogen, are most of them very incorrect. Thus his number for nitrogen was 5 instead of 4·67, that for carbon 5 instead of 6, that for oxygen 7 instead of 8, that for phosphorus 9 instead of 10·33, that for sulphur 13 instead of 16, and similarly with the remainder. Davy raised the number for oxygen from 7 to 7·5, which Prout, soon after, on theoretical grounds increased to 8. But the first series of numbers, deduced from trustworthy experiments, was drawn up by Berzelius, whose results, the work of a lifetime, must ever excite our highest admiration for the marvellous industry and skill by which they were achieved. Of late years, when analytical and synthetical processes have been so greatly simplified and improved, many of his atomic weights have undergone slight corrections at the hands of Dumas, Marignac, Pelouze, Stas, Maumené, Erdmann, Marchand, and others, but the general exactitude of his numbers still remains unimpeached. Berzelius, following the example of Wollaston in this country, selected the atomic weight of oxygen as the unit of his scale, and the same plan was adopted until within this last twenty years by continental chemists in general. The atomic weight of oxygen was fixed at 100, and those of the other elements estimated in accordance therewith; but the simpler numbers by which most of the ratios are expressed on the hydrogen scale, have eventually secured for it the preference.

In the year 1815, Prout, in a paper "on the relations between the specific gravities of bodies in the gaseous state, and the weights of their atoms," propounded the idea that the atomic weights of all bodies are multiples of the atomic weight of hydrogen. His opinion was shared by Dalton on other grounds, and met with very general acceptance in this country. But it was never acknowledged by Berzelius, or until lately by any large number of continental chemists. Although Prout's views must be considered, in the present state of our knowledge, to rest rather upon a speculative than a substantial philosophical basis, it cannot be denied that the tendency of modern investigation has been to confirm his law or rather a certain modification of it, which Dumas first introduced in a definite form, but which Prout himself seems to have admitted. According to this modification, the atomic weights of all bodies are multiples by whole numbers of a submultiple of the atomic weight of hydrogen. A striking confirmation of this view occurred in the year 1840, when Dumas and Stas showed that the atomic weight of carbon is exactly 6. In 1843 Dumas also showed that oxygen and hydrogen unite to form water exactly in the ratio of 8 to 1, and his experiments were confirmed by those of Erdmann and Marchand. Then Pelouze and Marignac separately ascertained that the atomic weight of nitrogen is 14; and Maumené, Marignac, and Pelouze, separately ascertained that the atomic weights of chlorine, silver, and potassium coincide almost absolutely with the numbers of 35·5, 108, and 39 respectively. Pelouze showed also that the atomic weights of sodium, barium, and arsenic are 23, 68·5, and 75 respectively. At the present time, out of fifty-eight elementary atomic weights, calculated from the acknowledged best experiments, not more than half a dozen differ appreciably from multiples by whole numbers of half the atomic weight of hydrogen. Some of these exceptional numbers ought probably to be doubled, whereby they would accord with Prout's modified law, while others of them can hardly be looked upon as satisfactorily determined. It is worthy of observation also that the smallest atomic weights which, as a general rule, are those of the best known, and most easily estimated elements, accord the most precisely with Prout's law. Dumas is of opinion that some of the exceptional numbers are multiples of one-fourth the atomic weight of hydrogen. Stas, from an elaborate series of experiments, the exactness of which it seems impossible to exceed, has arrived at the conclusion that Prout's law is not true, or at any rate that it is only approximatively true. He has obtained the following numbers for potassium, sodium, silver, sulphur, nitrogen, chlorine, and lead. Each number has been derived from numerous closely concordant experiments performed by different processes, on a scale of magnitude and with a degree of delicacy, hitherto unequalled. His number for potassium, however, is the only one which differs considerably *i.e.* $\frac{1}{3}$ per cent. from the usually accepted number:

		Stas's numbers.	Differences.
Potassium	39	39·130	+ 0·130
Sodium	23	23·050	+ 0·050
Silver	108	107·943	− 0·057
Sulphur	32	32·074	+ 0·074
Nitrogen	14	14·041	+ 0·041
Chlorine	35·5	35·460	− 0·040
Lead	103·5	103·457	− 0·043

Hence it is apparent that the differences in the experimental determination of the ratios according to which bodies combine with one another, have been reduced within very narrow limits. But the case is far otherwise when we come to consider the interpretation of these ratios, or the establishment of the atomic weights of simple and compound bodies. Thus mercury unites with chlorine in two proportions to form calomel and corrosive sublimate respectively. In the former compound the ratio of chlorine to mercury is as 35·5 to 200; and in the latter as 35·5 to 100; or as *twice* 35·5 to 200. We have therefore to decide between the numbers 200 and 100, wherewith to express the atomic weight of mercury. If we select the number 200, the formula of calomel will be $HgCl$, and that of corrosive sublimate $HgCl^{2}$. If we select the number 100, the formula of calomel will be $Hg^{2}Cl$, and that of corrosive sublimate, $HgCl$. Much the same difficulty also exists in those cases in which two elements combine in only one proportion. Thus chlorine unites with silver in the proportion of 35·5 to 108, or to *twice* 54. Now supposing even that we all agree to represent calomel by $Hg^{2}Cl$, and corrosive sublimate by $HgCl$, we have still to consider whether chloride of silver is a body analogous to calomel or to corrosive sublimate, before we can decide upon representing it by the formula $Ag^{2}Cl$, in which $Ag = 54$, or by the formula $AgCl$, in which $Ag = 108$. Again, chlorine unites with aluminium in the single proportion of 35·5 parts of chlorine to 9 parts of aluminium. Chloride of aluminium may consequently be represented by the formula $AlCl$, in which $Al = 9$; or by $AlCl^{2}$, in which $Al = 18$; or by $AlCl^{3}$, in which $Al = 27$; or by $Al^{2}Cl$, in which $Al = 4·5$; or by $Al^{2}Cl^{3}$, in which $Al = 13·5$; or by one of many other possible formulæ. From a variety of considerations, more or less complicated, the last formula, $Al^{2}Cl^{3}$, is the one which has been generally but not unanimously adopted. Again, the composition of marsh-gas has been ascertained with the greatest certainty. The ratio of carbon to hydrogen is precisely as 3 to 1. Hence we may represent the gas by the formula CH in which the atomic weight of carbon = 3; or by the formula CH^{2}, in which $C = 6$; or by the formula CH^{3}, in which $C = 9$; or by the formula CH^{4}, in which $C = 12$; or we may represent the gas by the formula $C^{2}H^{4}$, in which $C = 6$; &c. &c. At the present time, all chemists are agreed that the molecule of marsh-gas contains four atoms of hydrogen, but they disagree as to whether it contains two atoms of carbon having each the value 6, or one atom of carbon only having the value 12.

It is obvious that the atomic weights of an element and of its combinations, should be selected so as to express the entire series of combinations by the simplest series of formulæ; so as best to accord with the chemical properties and metamorphoses of the bodies; so as best to illustrate their analogies with other bodies; and so as to be in relation with their physical properties, such as their specific volumes, specific heats, isomorphism, &c. Now it so happens that these different requirements, chemical and physical, are not always satisfied by one and the same number. Hence we have to subordinate requirements, much in the same manner that zoologists and botanists subordinate characters, and to select that atomic weight which fulfils the greatest number, or rather the most important of them. Many of the discrepancies which were formerly thought to exist between the numbers deduced respectively from chemical and physical considerations, have of late years been satisfactorily explained away; and we have every reason to believe that with increasing knowledge leading to higher generalisations, all such anomalies as at present exist will also disappear.

In a determination of the least indivisible combining proportion, or chemical atom of a body, it is clear that purely chemical considerations must be entitled to the greatest weight, and to some of these we will now direct our attention. If we examine marsh-gas, for instance, we soon perceive that its molecule contains four atoms of hydrogen; because we find ourselves able to displace one-fourth, or two-fourths, or three-fourths, or four-fourths of its hydrogen. In other words, we find that its hydrogen is divisible into four equal parts; and as the atom of hydrogen expresses the least indivisible part of hydrogen that can enter into a combination, it is evident that marsh gas must contain four of such parts, or four atoms, of hydrogen. Thus taking the formula $C^{r}H^{4}$ for marsh-gas, we have the following series of derivatives, the constitution of which could not be expressed, save by according four atoms of hydrogen to the molecule of the gas.

$C^{r}H^{4}$	Marsh-gas	$C^{r}H^{4}$.	
$C^{r}H^{3}Cl$	Chloride of methyl	$C^{r}H^{3}Na$	Sodium-methyl.
$C^{r}H^{2}Cl^{2}$	Dichloride of methylene	. .	
$C^{r}HCl^{3}$	Chloroform	$C^{r}HI^{3}$	Iodoform.
$C^{r}Cl^{4}$	Tetrachloride of carbon	. .	

Hence the metamorphoses of marsh-gas show that the most simple formula by which the ratio of its carbon and hydrogen can be expressed, namely, CH, is not the proper formula of the body. Again, the quantity of marsh-gas, which is the resultant of any reaction, cannot be expressed with less than four atoms of hydrogen. Thus, when acetic acid is decomposed by heat, we have the reaction, $C^{2rr}H^{4}O^{2} = C^{r}H^{4} + C^{r}O^{2}$. The quantity of carbon C^{r}, which unites with 4 pts. of hydrogen to form marsh-gas, unites with 32 pts. of oxygen to form carbonic anhydride; but whereas the quantity of hydrogen in marsh-gas is experimentally divisible into 4 pts., the quantity of oxygen in carbonic anhydride is experimentally divisible into 2 pts. only; so that while we represent marsh-gas by the formula $C^{r}H^{4}$, we represent carbonic anhydride by the formula $C^{r}O^{2}$, as will be again referred to.

The same class of chemical reasons which induce us to regard marsh-gas as tetrahydric, also induce us to regard ammonia as trihydric. In ammonia we can replace one-third, or two-thirds, or three-thirds of its hydrogen, but we cannot replace one-fourth, or two-fourths, or three-fourths. The hydrogen in marsh-gas being divisible into 4 equal parts, the hydrogen in ammonia is divisible into 3 equal parts only, and consequently the molecule of ammonia contains 3 indivisible proportions or atoms of hydrogen. We are acquainted with many ammonias in which one, two, and three-thirds of the hydrogen are displaced, for example:

$N^{r}H^{3}$	Ammonia.	$N^{r}HI^{2}$	Diniodamide
$N^{r}H^{2}K$	Potassamine	$N^{r}Hg^{3}$	Trimercuramine, &c. &c.

But the most striking illustration of displacement by thirds is afforded by Hofmann's researches on the volatile alkaloids, in which he successively displaced one, two, and three atoms of hydrogen in ammonia by a mere continuation of one and the same process:

Ammonia.	Ethylia.	Diethylia.	Triethylia.	Ethyl-methyl-aniline.
$N^{r}\left\{\begin{matrix}H\\H\\H\end{matrix}\right.$	$N^{r}\left\{\begin{matrix}H\\H\\Et\end{matrix}\right.$	$N^{r}\left\{\begin{matrix}H\\Et\\Et\end{matrix}\right.$	$N^{r}\left\{\begin{matrix}Et\\Et\\Et\end{matrix}\right.$	$N^{r}\left\{\begin{matrix}Et\\Me\\Ph\end{matrix}\right.$ &c. &c.

Again, in ninety-nine cases out of a hundred, the quantity of ammonia which is the agent or resultant of a reaction, must contain 3 or some multiple of 3 atoms of hydrogen. Thus when ammonia results from the hydrogenation of nitric acid, we obtain, for every molecule of nitric acid containing 1 atom of hydrogen, a quantity of ammonia containing 3 atoms; and when ammonia reacts with benzoic chloraldehyde to form benzamide and sal-ammoniac, we require, for every molecule of benzoic chloraldehyde decomposed, a quantity of ammonia containing *twice* 3 atoms of hydrogen, $2N^{r}H^{3}$; and so in other instances. In the great majority also of compounds which ammonia forms directly with other bodies, the quantity of combining ammonia must necessarily be represented with 3 or some multiple of 3 atoms of hydrogen. Thus the single molecule of aldehyde unites with $N^{r}H^{3}$, and the single molecule of nitrate of silver with $2N^{r}H^{3}$. &c. Express these combinations or reactions how we please, we cannot represent them save with a proportion of ammonia containing 3 or some multiple of 3 atoms of hydrogen, and ninety-nine cases out of a hundred will yield the same result. In those few exceptional cases in which the combining or reacting ammonia need not necessarily be represented with 3 atoms of hydrogen, it may be, and we contend ought to be, so represented. Thus when ammonia is decomposed by excess of chlorine, the reaction might be expressed, thus: $\overset{r}{N}^{3} + Cl = \overset{r}{N}^{5}Cl + HCl$: but it is quite certain that the molecule of chloride of nitrogen contains 3 at. of chlorine, and consequently the reaction by which it is produced ought to be expressed thus: $N^x H^3 + Cl^6 = N^x Cl^3 + 3HCl$; and so in other instances.

The same class of chemical reasons which induce us to regard marsh-gas as tetrahydric and ammonia as trihydric, also induce us to regard water as dihydric. In water we can replace one-half or two-halves of the hydrogen, but we cannot replace one-third or two-thirds as in ammonia, or one-fourth or three-fourths as in marsh-gas. If we act upon water $O^x H^2$ by metallic potassium, we displace one-half its hydrogen to form the very definite body *hydrate of potassium* $O^x KH$; and if we act upon hydrate of potassium by potassium, we displace the other half of the hydrogen and form *oxide of potassium* $O^x KK$. Or instead of introducing a second atom of potassium, we may turn out the first one. Thus if we treat hydrate of potassium $O^x KH$ with iodide of ethyl we obtain *alcohol* $O^x EtH$, or we put a molecular grouping called ethyl in the place of the potassium, which displaced one-half the hydrogen of the water. Now if we act upon the alcohol thus formed by potassium, it behaves exactly as did the hydrate of potassium, or in other words it yields the remaining half of the original hydrogen in exchange for potassium, and we obtain *ethylate of potassium* $O^x EtK$. If we now act upon this new body by the iodide of methyl or ethyl, we turn out the potassium representing one-half the original hydrogen and obtain *ethylate of methyl* $O^x EtMe$, or *ethylate of ethyl* $O^x EtEt$.

Again, in ninety-nine cases out of a hundred, the quantity of water, which is the agent or resultant of a reaction must contain 2 or some multiple of 2 atoms of hydrogen. Thus, whenever an alcohol, ketone, or any definite organic substance, yields a hydrocarbon or other compound by dehydration,—whenever an organic acid yields a pyroacid, or other pyrogenous product by dehydration,—whenever a salt of ammonia, phenylamine, or other volatile alkali loses water,—and whenever two compounds act upon one another to form a new body with simultaneous elimination of water, whether the action be that of an acid upon a hydrocarbon, of an acid upon an alcohol, of an acid upon an alkali, of an acid upon an acid, of an acid upon an aldehyde, of an alkali upon an aldehyde, or of an alkali upon an alcohol,—the quantity of water eliminated inevitably contains 2, or some multiple of 2 atoms of hydrogen. Moreover whenever a conjugated compound or diameride, a chloraldehyde, an organometallic body, &c. &c., is decomposed by water, the quantity of water which reacts must necessarily be represented with 2 or some multiple of 2 atoms of hydrogen. For example, when water reacts with hippuric acid to form benzoic acid and glycocine, for every molecule of hippuric acid decomposed, we require a quantity of water containing $O^x H^2$. When glycerin becomes acrolein by dehydration, for every molecule of glycerin decomposed we obtain a quantity of water containing $2O^x H^2$. When nitric acid reacts with naphthalene to form nitro-naphthalene, for every molecule of nitric acid which reacts, we have eliminated a quantity of water containing $O^x H^2$. When acetate of ammonia becomes cyanide of methyl by loss of water, for every molecule of the salt decomposed, we liberate a quantity of water containing $2O^x H^2$; and so in an infinite number of other instances. Again, in the majority of direct compounds which water forms with other bodies, the combining water must be represented with two atoms, or some multiple of two atoms of hydrogen. Thus the molecule of glucose differs from that of fructose, and that of lactine differs from that of dextrine by the addition of $O^x H^2$. The molecule of turpentine becomes hydrated turpentine by absorbing $3O^x H^2$, and so in many other instances. The water of crystallisation in the great majority of hydrated salts must be represented with 2 atoms, or some multiple of 2 atoms of hydrogen. Thus the molecules of chloride of barium, nitrate of mercurosum, and chloride of copper, crystallise with $O^x H^4$; the molecules of nitrate of cadmium, chloride of manganese, and nitrate of calcium with $2O^x H^4$; the molecules of chloride of calcium, nitrate of magnesium, and acetate of sodium with $3O^x H^2$; the molecules of microcosmic salt and hydrate of barium with $4O^x H^2$; the molecule of borax with $5O^x H^2$; the molecules of chloride of aluminium and potassio-sulphate of nickel, with $6O^x H^2$; the molecule of common arsenate of sodium with 7 or 12 $O^x H^2$; and the molecules of alum and rhombic phosphate of sodium with $12O^x H^2$, &c. &c. There are some comparatively few salts, the acetate of barium, for example, in which the water of crystallisation might be represented by $\frac{1}{2}O^x H^2$, or by $1\frac{1}{2}O^x H^2$, &c., but none in which it need be so represented, while there are scarcely any reactions in which the resulting or reacting water could possibly be expressed by $\frac{1}{2}O^x H^2$ or $1\frac{1}{2}O^x H^2$, and none in which it would be correctly so expressed.

We have mentioned above that the quantity of carbon which unites with four separable portions of hydrogen to form marsh-gas, also unites with two separable portions of oxygen to form carbonic anhydride. Now each of these separable portions of oxygen is identical with the quantity of oxygen O^x, which unites with 2 parts of hydrogen to form water.

Lastly, when we come to examine hydrochloric acid, we are unable to show that its hydrogen is divisible, and we consequently look upon its molecule as containing but one atom, or one indivisible proportion of hydrogen; whence we represent the compound by the formula $Cl^{x}H$; and we may anticipate here by remarking, that all physical evidence tends to show that the molecules of marsh-gas, ammonia, water, and chlorhydric acid contain respectively four, three, two, and one atom of hydrogen.

In addition to the class of binary hydrides, the atomic weights of the principal members of which we have just considered, there is another large class of hydrogenised bodies, namely, the class of ternary or oxacids, the correct determination of whose molecules is of the highest importance. The molecule of oxalic acid, for instance, may be represented by the formula $C^{x}HO^{2\times x}$, or $C^{2\times x}H^{2}O^{4\times x}$, according as the acid is found to be monhydric or dihydric, monobasic or dibasic. Now the polybasicity of an acid does not depend in any way upon the indivisibility of its formula, but solely upon its possession of certain specific characters; and the examination of the properties of oxalic acid soon shows us that its molecule must be represented, not by the more simple monobasic, but by the more complex dibasic formula. In fact the same class of chemical reasons which induce us to regard water as dihydric, must also induce us to regard oxalic acid as dihydric, and so in other instances. Inasmuch as the modes of distinguishing between monobasic, dibasic, tribasic, and tetrabasic acids have been minutely set forth in the article ACIDS, it is unnecessary here to repeat them. We will only observe that certain special acids, to the properties and metamorphoses of which we shall presently have occasion to advert, are proved by their specific characters to be dihydric and dibasic, namely:

Carbonic acid	$H^{2}C^{x}O^{3\times x}$
Oxalic acid	$H^{2}C^{x}O^{4\times x}$
Sulphurous acid	$H^{2}S^{x}O^{3\times x}$
Sulphuric acid	$H^{2}S^{x}O^{4\times x}$

We will now turn our attention to the atomic weights of the four elements with which the hydrogen of the four primary hydrides, whose atomic weights we have considered somewhat minutely, is combined; whereby it will appear that the quantities of carbon, nitrogen, oxygen, and chlorine which we have represented by the symbols C^{x}, N^{x}, O^{x}, and Cl^{x}, respectively, constitute the atoms of these elements, or the smallest indivisible proportions of them which can enter into chemical combination. To begin with carbon: we wish to prove that 12 parts of that element, or the quantity thereof which combines with 4 parts of hydrogen to form marsh-gas, is the smallest proportion of carbon that can exist in a compound. We find in the first place that the quantity of carbon contained in the great majority of carbon-compounds must necessarily be represented by 12, or some multiple of 12 parts. We may adduce in illustration of this position, the primary series of homologous fatty acids and their sodium-salts.

Formic	$C^{1\times 12}H^{2}O^{2\times x}$	$C^{1\times 12}H\ NaO^{x\times 2}$	Formate
Acetic	$C^{2\times 12}H^{4}O^{2\times x}$	$C^{2\times 12}H^{3}NaO^{x\times 2}$	Acetate
Propionic	$C^{3\times 12}H^{6}O^{2\times x}$	$C^{3\times 12}H^{5}NaO^{x\times 2}$	Propionate
Butyric	$C^{4\times 12}H^{8}O^{2\times x}$	$C^{4\times 12}H^{7}NaO^{x\times 2}$	Butyrate
Valeric	$C^{5\times 12}H^{10}O^{2\times x}$	$C^{5\times 12}H^{9}NaO^{x\times 2}$	Valerate
Caproic	$C^{6\times 12}H^{12}O^{2\times x}$	$C^{6\times 12}H^{11}NaO^{x\times 2}$	Caproate

The ratio of carbon to hydrogen in the sodium-salts, necessitates our expressing the constituent carbon as a multiple of 12. The mere ratio of carbon to hydrogen in the acids, would allow the carbon, in all of them, to be expressed satisfactorily by numbers which are not multiples of 12, but of 6. Valeric acid, for instance, might be represented by the formula $C^{5\times 6}H^{5}O^{x}$; but the circumstance that one-tenth part of its hydrogen can be displaced by sodium prevents the possibility of our halving the hydrogen in its molecule, and consequently of our reducing its carbon from a multiple of 12 to a mere multiple of 6.

From the circumstance that all carbon-compounds must be represented with 12 parts, or some multiple of 12 parts of carbon, it follows that whenever two compounds differ from one another by the different proportions of carbon which they respectively contain, that difference amounts to 12 parts of carbon, or to some multiple of 12 parts. Thus, *wood-spirit* consists of 16 pts. of oxygen, 4 pts. of hydrogen, and 12 pts. of carbon, whereas in *aldehyde* we have another 12 parts of carbon, and in *acrolein* two other 12 parts of carbon in addition, so that the three bodies may be represented by the respective formulæ:

$C^{1\times 12}H^{4}O^{x}$	Wood-spirit
$C^{2\times 12}H^{4}O^{x}$	Aldehyde
$C^{3\times 12}H^{4}O^{x}$	Acrolein

We are not acquainted with any bodies intermediate in composition between wood-spirit and aldehyde, or between aldehyde and acrolein, nor have we any reason to anticipate their formation at any future time. Again *toluene* contains 8 parts of hydrogen united with seven times 12 parts of carbon; whereas *cinnamene* contains another 12 parts of carbon, and *naphthalene* three other 12 parts of carbon in addition, thus:

$C^{7\times12}H^8$	Toluene
$C^{8\times12}H^8$	Cinnamene
$C^{9\times12}H^8$	Wanting
$C^{10\times12}H^8$	Naphthalene

Now the probability amounts almost to a certainty that a hydrocarbon intermediate between cinnamene and naphthalene will be discovered, and that a hydrocarbon intermediate between toluene and cinnamene, or between cinnamene and the expected compound, or between the expected compound and naphthalene will not be discovered. It follows also that when carbon, plus some other element or elements, is added to or taken from a body, the quantity of carbon added or subtracted is always 12 parts, or some multiple of 12 parts. Thus the molecule of *sodium-ethyl* absorbs 12 parts of carbon, plus some oxygen to form *propionate of sodium; aconitic acid*, by the loss of 12 parts of carbon, plus some oxygen, becomes *citraconic acid*; and *phthalic* acid, by the loss of twice 12 parts of carbon, plus some oxygen, becomes *benzene*. Moreover in those series of compounds known as homologous, the quantity of carbon in each successive member of the series increases by 12 parts, as shown in a preceding table of the fatty acids and their sodium-salts. All chemists recognise the fact, which is indeed indisputable, that the smallest increment or decrement of carbon that can be effected in a compound is 12 times as great as the smallest quantity of hydrogen that can be introduced into or displaced from a compound; so that if the entire series of carbon-compounds is to be represented by the simplest satisfactory formulæ, the atom or smallest combining proportion of carbon must be represented as having 12 times the weight of the atom or smallest combining proportion of hydrogen. But some chemists who from old association still accord to carbon the atomic weight 6, consider that all carbon-compounds contain an even number of atoms of carbon, and that in the decompositions and recompositions of these compounds, two inseparable carbon-atoms are always concerned. But if we understand the smallest inseparable or indivisible proportion of an element to constitute its atom, the conception of two inseparably associated atoms is clearly illogical. Two small atoms of carbon, having each the value 6, if they can never be separated from each other, must nececessarily constitute one large atom of carbon having the value 12.

There are two well-known compounds of carbon, namely, carbonic oxide, and carbonic anhydride, which may possibly be regarded as constituting exceptions to some of our previously made assertions. Thus the molecules of these two bodies may be represented by one or other of the following pairs of formulæ:

$C^{1\times6}O^{1\times8}$	Carbonic oxide	$C^{1\times12}O^{1\times16}$
$C^{1\times6}O^{2\times8}$	Carbonic anhydride	$C^{1\times12}O^{2\times16}$

Now provided we recognise the dibasicity of the carbonic, oxalic, and other similar acids, as their chemical properties require us to do, it is quite certain that a proportion of either carbonic oxide or carbonic anhydride, containing only 6 parts of carbon, is incapable of effecting or of resulting from a definite chemical reaction. Carbonic anhydride in particular, is a very frequent product of chemical action, but in no definite decomposition do we ever obtain a smaller proportion of the gas than that represented by 12 parts of carbon plus 32 of oxygen. A few illustrations are appended of the formation of carbonic oxide and carbonic anhydride, from the decomposition by heat of three monobasic acids, namely, the formic, acetic, and benzoic; of two dibasic acids, namely, the oxalic and tartaric; and of one tribasic acid, namely, the aconitic, the decomposition of which last has been before referred to.

Formic acid	$C^{1\times12}H^2O^{2\times x} = C^{1\times12}O^{1\times x} + H^2O$
Acetic acid	$C^{2\times12}H^4O^{2\times x} = C^{1\times12}O^{2\times x} + C^{1\times12}H^4$
Oxalic acid	$C^{2\times12}H^2O^{4\times x} = C^{1\times12}O^{1\times x} + C^{1\times12}O^{2\times x} + H^2O^x$
Benzoic acid	$C^{7\times12}H^6O^{2\times x} = C^{1\times12}O^{2\times x} + C^{6\times12}H^6$
Tartaric acid	$C^{4\times12}H^6O^{6\times x} = C^{1\times12}O^{2\times x} + C^{3\times12}H^4O^{3\times x} + H^2O^x$
Aconitic acid	$C^{6\times12}H^4O^{6\times x} = C^{1\times12}O^{2\times x} + C^{5\times12}H^4O^{4\times x}$.

With regard to nitrogen, all chemists are agreed that 14 parts of that element, or the quantity thereof which combines with 3 parts of nitrogen to form ammonia, is the smallest proportion of nitrogen that can exist in a combination. We find that the quantity of nitrogen contained in the great majority of nitrogenous compounds, including all salts of ammonia and of organic alkaloïds, must necessarily be represented by 14 parts, or some multiple of 14 parts. Among miscellaneous bodies we may adduce cyanogen, indigo, and nitric acid, each of which contains 14 parts of nitrogen; urea, asparagin, and chrysammic acid, each of which contains twice 14 parts of nitrogen; creatine and carbazotic acid, each of which contains three times 14 parts of nitrogen; uric acid and caffeine, each of which contains four times 14 parts of nitrogen, &c. &c. From the circumstance that all nitrogenous compounds must be represented with 14 parts of nitrogen, it follows that whenever nitrogen is liberated by a chemical reaction, and whenever nitrogen plus some other element is introduced into a chemical compound, the quantity of nitrogen concerned must be represented by 14 parts or some multiple of 14 parts. Thus by the action of nitric acid upon the hydrocarbons, and upon a great variety of other compounds, we can introduce into the compounds 14 parts, or twice 14 parts, or three times 14 parts, &c. &c. of nitrogen, whereas we cannot introduce any intermediate proportion. Again, when sal-ammoniac is decomposed by chlorine, for every molecule of the salt decomposed, 14 parts of nitrogen are liberated; and when nitrate of ammonia is decomposed by metallic zinc, for every molecule of the salt decomposed twice 14 parts of nitrogen are liberated; and so on. There are a few bodies formed on the type of one or more atoms of ammonia, in which the ratios of the constituent elements might be satisfactorily expressed by formulæ in which the quantity of nitrogen represented was not a multiple of 14. Thus trimercuramine might be represented by the formula $N^{1\times4\cdot7}Hg$, and triethylamine, by the formula $N^{1\times4\cdot7}C^2H^5$. Similarly, all derivatives of ammonia in which the whole of the hydrogen is displaced by one and the same metal, hydrocarbon, or halogen, might be represented by formulæ in which $N = 4\cdot7$; which formulæ moreover, would be more simple than those in which $N = 14$. But the same class of reasons which induce us to represent the molecule of ammonia with 3 atoms of hydrogen, induce us to represent the molecules of these bodies with 3 atoms of metal, radicle, or halogen. Thus triethylamine is the third of a series of compounds, namely, $N^{1\times14}H^2(C^2H^5)$, $N^{1\times14}H^1(C^2H^5)^2$, and $N^{1\times14}(C^2H^5)^3$, obtained successively by a continuance of the same reaction. Moreover, a quantity of triethylamine containing less than 14 parts of nitrogen, is not sufficient to effect any decomposition, or to combine with the molecule of any acid or salt. It is observable that the entire series of compounds is represented most simply by formulæ, in which $N = 14$, although one particular member of the series may be represented most simply by a formula in which $N = 4\cdot7$.

Let us now direct our attention to oxygen. We wish to show that 16 parts of that element, or the quantity thereof which unites with 2 atoms of hydrogen to form water, is the smallest proportion of oxygen that can enter into a combination. We find in the first place that the quantity of oxygen contained in the great majority of definite oxidised compounds, must necessarily be represented by 16 or some multiple of 16 parts. Thus the molecules of all hydrates, double oxides, acids, oxisalts, aldehydes, ketones, alcohols, oxacid-ethers, and a great number and variety of other compounds, doubtless forming together 99 per cent. of all known compounds of oxygen, cannot be represented save with 16 parts, or some multiple of 16 parts of oxygen. For example, the molecules of *hydrate of potassium*, *benzoic aldehyde*, *acetone*, *chloral*, *hypochlorite of sodium*, &c. &c. each contain 16 parts of oxygen. The molecules of *spinelle*, *brown-hæmatite*, *camphor*, *benzile*, *acetate of sodium*, *benzoic acid*, &c. &c. each contain twice 16 parts of oxygen. The molecules of *nitric acid*, *glycerin*, *chlorate of potassium*, *salicylic acid*, *augite*, &c. &c. each contain three times 16 parts of oxygen. The molecules of *phosphate of sodium*, *perchloric ether*, *garnet*, *olivine*, *sulphovinic acid*, &c. &c. each contain four times 16 parts of oxygen. The molecules of *starch*, *acid malate of lead*, *nitrosalicylic acid*, &c. &c. each contain five times 16 parts of oxygen. The molecules of *mannite*, *cream of tartar*, &c. &c. each contain six times 16 parts of oxygen, while the molecules of *citric acid*, *pyrophosphate of copper and sodium*, &c. &c. contain each seven times 16 parts of oxygen, and so on. From the circumstance that nearly all oxidised compounds must necessarily be represented with 16 or some multiple of sixteen parts of oxygen, it follows that when two bodies differ from one another in composition by the different proportions of oxygen which they respectively contain, that difference amounts to 16 parts or some multiple of 16 parts of oxygen, as is well seen in the two following series of bodies.

KCl	Chloride of potassium	C^2H^4	Ethylene
$KClO^{1\times16}$	Hypochlorite of potassium	$C^2H^4O^{1\times16}$	Aldehyd
$KClO^{2\times16}$	Chlorite of potassium	$C^2H^4O^{2\times16}$	Acetic acid
$KClO^{3\times16}$	Chlorate of potassium	$C^2H^4O^{3\times16}$	Glycolic acid
$KClO^{4\times16}$	Perchlorate of potassium	$C^2H^4O^{4\times16}$	Glyoxylic acid.

It follows also that the quantity of oxygen which can be liberated by any reaction, and which, either alone or together with some other element, can be added to, substracted from, or displaced in a compound, must be 16 or some multiple of 16 parts. Now why this should be unless the 16 parts constitute an indivisible proportion or chemical atom, is quite inconceivable. We may adduce the following illustrations. Each molecule of nitrate of sodium decomposed by heat into oxygen and nitrite of sodium, yields 16 parts of oxygen. Each molecule of permanganate of potassium, decomposed by sulphuric acid into oxygen and manganese-alum, yields twice 16 parts of oxygen. Each molecule of chlorate of potassium decomposed by heat into oxygen and chloride of potassium, yields three times 16 parts of oxygen. Each molecule of pentachloride of phosphorus, converted by treatment with water into phosphoric chloraldehyde and hydrochloric acid, acquires 16 parts of oxygen in exchange for an equivalent quantity of chlorine. Each atom of alcohol converted into aldehyde by oxidation, reacts with 16 parts of oxygen, and each atom of alcohol converted into acetic acid by oxidation, reacts with twice 16 parts of oxygen. Each molecule of bromacetic acid, converted by the action of water into glycolic acid, acquires 16 parts of oxygen and 1 part of hydrogen, in exchange for one atom of bromine. Each atom of benzene, converted by treatment with nitric acid into nitrobenzene, acquires twice 16 parts of oxygen, and 14 parts of nitrogen, in exchange for one atom of hydrogen, and so on. But precisely as there are some nitrogenised bodies which with the atomic weight of nitrogen = 4·7, may be divided into thirds, and can thus receive simpler formulæ than with the atomic weight of nitrogen = 14; so are there some comparatively few oxidised bodies which, with the atomic weight of oxygen = 8, may be divided into halves, and can thus receive simpler formulæ than with the atomic weight of oxygen = 16. We have seen, however, that if the comparable molecules of nitrogenised bodies were correctly formulated they would all be represented more simply by formulæ in which N = 14, than by formulæ in which N = 4·7; so it will appear that if the comparable molecules of oxidised bodies were correctly formulated, they would all be represented more simply by formulæ in which O = 16, than by formulæ in which O = 8. Those oxidised bodies in which the ratio of the oxygen to the other constituents can be satisfactorily expressed by assigning to the oxygen a number which is not 16 or a multiple of 16, but only 8 or a multiple of 8, comprise most compounds in which the oxygen is united with one kind of matter only, including all the simple metallic oxides. Thus in water and lime, the ratio of the constituent oxygen to the hydrogen and calcium respectively, is as satisfactorily expressed by the formulæ $O^{1\times 8}H$, and $O^{1\times 8}Ca$, as by the formulæ $O^{1\times 16}H^2$, and $O^{1\times 16}Ca^2$. The only question is, which of these pairs of formulæ represents the molecules of the two bodies. Now it is no more necessary to argue the point whether $O^{1\times 8}Ca$, is the correct expression for the metallic oxide, lime, than it was to argue the point whether $N^{1\times 4\cdot 7}Hg$, was the correct expression for the metallic nitride, mercuramine. The accordance of a trihydric formula to ammonia, necessitates the accordance of a trimetallic formula to mercuramine, and in a precisely similar manner, the accordance of a dihydric formula to water necessitates the accordance of a dimetallic formula to lime. It may be observed, moreover, that many strictly comparable reactions can be effected by means of water, hydrate of calcium, and lime respectively, and that in these cases the quantities of the reagents can only be expressed by the formulæ $O^{1\times 16}HH$, $O^{1\times 16}HCa$, and $O^{1\times 16}CaCa$. Again, in bodies analogous to ordinary ether and the homogeneous anhydrides, the ratio of the oxygen to the other constituents may be satisfactorily represented by formulæ in which the proportion of oxygen is expressed by 8 parts only. Thus ether may be represented by the formula $O^{1\times 8}Et$, and benzoic anhydride by the formula $O^{1\times 8}Bz$; but all arguments founded on mode of formation, on reactions, on vapour-densities, on seriated position and properties, &c. tend to show that the above formulæ are not correct expressions of the molecules of the bodies represented, which, like that of water, contain 16 parts of oxygen. Thus, ether is one of the following series of bodies: $O^{1\times 16}HEt$, ethylate of hydrogen, or alcohol; $O^{1\times 16}MeEt$, ethylate of methyl; $O^{1\times 16}EtEt$, ethylate of ethyl or ether; $O^{1\times 16}PrEt$, ethylate of propyl; and benzoic anhydride is one of the following series. $O^{1\times 16}HBz$, benzoate of hydrogen, or benzoic acid; $O^{1\times 16}BzBz$, benzoate of benzoyl, or benzoic anhydride; $O^{\times 16}AcBz$, benzoate of acetyl, or aceto-benzoic anhydride; &c. &c. Lastly, in certain dibasic acids and their salts of one metal, the ratio of the oxygen to the other constituents may be satisfactorily expressed by monobasic formulæ, in which the oxygen is expressed not as a multiple of 16, but as a multiple of 8. Thus sulphurous acid and sulphite of sodium may be formulated as follows: $HS^{\overset{\prime\prime}{\frac{1}{2}}}O^{3\times 8}$, and $NaS^{\overset{\prime\prime}{\frac{1}{2}}}O^{3\times 8}$, respectively. But as we have before observed, the distinctions between monobasic and dibasic acids and their salts are very decided; and inasmuch as these acids and salts are indisputably dibasic (see ACIDS), their molecules cannot be correctly represented by monobasic formulæ. The simplest dibasic formulæ for carbonates, sulphites, and sulphates respectively, are the following, in which the proportion of oxygen is necessarily expressed as a multiple of 16 parts:

$H^2CO^{3\times16}$	$H^2S^{=}O^{3\times16}$	$H^2S^{=}O^{4\times16}$
$CaHCO^{3\times16}$	$NaHS^{=}O^{3\times16}$	$KHS^{=}O^{4\times16}$
$Ca^2CO^{3\times16}$	$Na^2S^{=}O^{3\times16}$	$K^2S^{=}O^{4\times16}$
$MgCaCO^{3\times16}$	$NH^4NaS^{=}O^{3\times16}$	$NiKS^{=}O^{4\times16}$

Many chemists, who acknowledge that the molecule of water consists of 2 parts of hydrogen united with 16 pts. of oxygen, and that, in ninety-nine cases out of a hundred, the smallest quantity of oxygen that can enter into the composition of a well-defined molecule must be represented by 16 parts, prefer, from old association, to accord to oxygen the atomic weight 8, and to admit that all oxygenated molecules contain two inseparably associated atoms of oxygen, or some multiple of two inseparably associated atoms. Thus, they represent water by the formula $H^2O^{2\times8}$ instead of H^2O, and nitric acid by $HNO^{6\times8}$ instead of HNO^3, &c. This practice is evidently most inconsequent: for the conception of two inseparable proportions of 8 each, amounts after all to that of one indivisible proportion of 16, that is to an atomic proportion of 16. To be consistent, we must represent the molecules of hydrochloric acid, water, ammonia, and marsh-gas either by Gerhardt's atomic, or by Dalton's equivalent formulæ, thus:

$HCl^{1\times35\cdot5}$	Hydrochloric acid	$HCl^{1\times35\cdot5}$
$H^2O^{1\times16}$	Water	$HO^{1\times8}$
$H^3N^{1\times14}$	Ammonia	$HN^{1\times4\cdot7}$
$H^4C^{1\times12}$	Marsh-gas	$HC^{1\times3}$

except that Dalton took, not marsh-gas, but olefiant-gas, for his standard hydrocarbon, and accorded to it the formula $HC^{1\times6}$, whereby marsh-gas became $H^2C^{1\times6}$. Now-a-days we know that the molecules of marsh-gas and olefiant-gas both contain the same number of hydrogen-atoms, and that their formulæ are $C^{1\times16}H^4$ and $C^{2\times16}H^4$ respectively.

With regard to chlorine, all chemists are agreed that 35·5 parts of that element, or the quantity thereof which unites with 1 part of hydrogen to form hydrochloric acid, is the smallest quantity of chlorine that can enter into a combination. We find that 35·5 parts of chlorine are capable of directly displacing 1 part of hydrogen in a great variety of compounds; that in all well defined molecules, the quantity of constituent chlorine must be represented by 35·5, or some multiple of 35·5 parts; that whenever two bodies differ from one another in composition by the quantity of chlorine they respectively contain, the difference amounts to 35·5, or some multiple of 35·5 parts; and that it is impossible to add to, subtract from, or displace in any compound a proportion of chlorine which is not represented by 35·5, or some multiple of 35·5 parts.

In the course of the preceding observations, reference has occasionally been made to the principle of analogy as a guide in determining the molecule of a compound body, and the atomic weights of its constituent elements. Thus we have referred to the analogy of triethylamine with ammonia, and to that of lime or oxide of calcium with water or oxide of hydrogen. But, in addition to the arguments already used, we may show more especially that the principle of analogy is in favour of the atomic weights and molecules which we have adopted. Thus the indisputable analogies of nitrous acid, nitric acid, and peroxide of nitrogen, with chlorous acid, chloric acid, and peroxide of chlorine respectively, are shown very clearly by formulæ in which $N = 14$, whereas they would be concealed by formulæ in which $N = 4\cdot7$, as seen below:

Chlorous acid,	$HClO^2$	HNO^2	Nitrous acid	HN^3O^2
Chloric acid,	$HClO^3$	HNO^3	Nitric acid	HN^3O^3
Perchloric oxide,	Cl^2O^4	N^2O^4	Pernitric oxide	N^6O^4

Again, with the molecule of water = 9, the relation of water to the alcohols as the undoubted vanishing term of the series, would not be manifested as it is with the molecule = 18. Thus, if we write alcohol $C^2H^6O^{2\times8}$, wood-spirit $CH^4O^{2\times8}$, and water $HO^{1\times8}$, the relation of water to the alcohols does not appear, but in the following series of formulæ with $O = 16$, it is perfectly apparent:

$C^5H^{12}O$, Amylic alcohol	C^2H^6O, Ethylic alcohol
$C^4H^{10}O$, Butylic „	CH^4O, Methylic „
C^3H^8O, Propylic „	H^2O, Hydric „

The relation of water to the alcohols, as shown in the above formulæ, is not a mere paper relation, but has its foundation in experiment. When water and alcohol respectively are acted upon by potassium, by chloride of benzoyl, by pentachloride of phosphorus, and by a host of other reagents, the reactions are acknowledged by all to be precisely similar. All chemists, no matter what the formulæ they employ, recognise the fact that the quantity of water which in a reaction corresponds to one proportion of alcohol, must contain two units of hydrogen. Similarly, with regard to hydrated bases and acids. The reactions of the bodies clearly show that the quantity of water which corresponds to one proportion of hydrate of potassium, or of hypochlorous acid, for instance, must contain two units of hydrogen. If we write hydrate of potassium $KHO^{2\times 8}$, hypochlorous acid $HClO^{2\times 8}$, and water $HO^{1\times 8}$, the formulæ do not represent comparable quantities. But, in the following series of formulæ with O = 16, the relations of the bodies are rendered perfectly evident:

KKO, Oxide of potassium	HClO, Hypochlorous acid
KHO, Hydrate of potassium	ClClO, Hypochlorous anhydride
HHO, Water	KClO, Hypochlorite of potassium

Moreover the principle of analogy is frequently allowed to overrule all other considerations. Thus the smallest quantity of aluminium that can enter into a combination is 27·5 times as great as the smallest quantity of hydrogen. This quantity of aluminium, like 14 parts of nitrogen, is capable of uniting with 3 atoms of chlorine, and of its representatives. But, from the strong analogy existing between aluminic and ferric compounds, the atomic weight of aluminium is fixed at 13·75, in order that its compounds may be represented by formulæ which, though more complex than those with Al = 27·5, are in accordance with the formulæ of corresponding ferric compounds, thus:

Fe^2Cl^3,	Sesquichloride of iron
$KFe^2(SO^4)^2 . 12H^2O$,	Iron alum
HFe^2O^2,	Brown hæmatite
Al^2Cl^3,	Sesquichloride of aluminium
$KAl^2(SO^4)^2 . 12H^2O$,	Common alum
HAl^2O^2,	Diaspore

The principle of analogy frequently enables us to determine satisfactorily the molecules and atomic weights of bodies with which we are comparatively but little acquainted. Thus the analogy of selenium and tellurium compounds, in so far as they are known, to the well-known compounds of sulphur, requires us to give similar formulæ to the similar compounds of all three elements. With regard to sulphur itself, precisely the same reasons that induce us to represent water by the formula H^2O, and to accord to oxygen the atomic weight 16, must induce us to represent sulphydric acid by the formula H^2S, and to accord to sulphur the atomic weight 32. But even if our acquaintance with sulphur were much less intimate than it is, still the analogy of its best known compounds with those of oxygen would suffice to allow of a satisfactory determination of its atomic weight. The principle of analogy induces us to accord to the primary hydrides and chlorides of the more or less electronegative elements, the following formulæ, and to classify them in four principal groups, thus:

Monatomic.	Diatomic.	Triatomic.	Tetratomic.
HF	H^2O	H^3N	H^4C
HCl	H^2S	H^3P	H^4Si
HBr	H^2Se	H^3As	Cl^4C
HI	H^2Te	H^3Sb	Cl^4Si
ClI	Cl^2O	Cl^3N	Cl^4Sn
	Cl^2S	Cl^3P	
		Cl^3As	
		Cl^3Sb	
		Cl^3Bi	

The following table represents the atomic weights of the elementary bodies on the hydrogen scale (H = 1) as determined by the preceding considerations. Those on the oxygen-scale (O = 100), which are now but little used, may be found by multiplying the hydrogen-numbers by $\frac{100}{16}$ or 6·25. The actual determinations of the atomic weights are given, with the methods of quantitative estimation, under each element.

Table of Atomic Weights.

Name.	Symbol.	Atomic Weight.	Formula of Compound analysed.	According to Experiments by
Aluminium . . .	Al	13·75	Chloride of aluminium, Al^2Cl^3	Dumas.
Antimony . . .	Sb	120·3	Trisulphide, Sb^2S^3	Schneider.
		122	Trichloride, $SbCl^3$	Dumas.
Arsenic	As	75	„ $AsCl^3$	Pelouze, Berzelius.
Barium	Ba	68·6	Chloride, BaCl	Marignac, Pelouze.
Bismuth	Bi	210	„ $BiCl^3$	Dumas.
Boron	B	11	Boric anhydride, B^2O^3	Berzelius.
			„ chloride, BCl^3	Dumas.

TABLE *continued.*

Name.	Symbol.	Atomic Weight.	Formula of Compound analysed.	According to Experiments by:
Bromine	Br	80	Bromide of potassium, KBr	Marignac.
Cadmium	Cd	56	Oxide, Cd^2O	Von Hauer.
Calcium	Ca	20	Lime, Ca^2O	Erdmann and Marchand.
Carbon	C	12	Carbonic anhydride, CO^2	Dumas and Stas. Erdmann and Marchand.
Cerium	Ce	46	Cerous oxide, Ce^2O	Marignac, Hermann.
Chlorine	Cl	35·5	Chloride of potassium „ „ silver	Marignac, Penny; Maumené, Berzelius. Dumas.
Chromium	Cr	26·2	Chromic anhydride, Cr^2O^3	Péligot, Berlin.
Cobalt	Co	29·5	Chloride, CoCl	Dumas.
Columbium or Niobium	Cb	97·6	Tetrachloride, $CbCl^4$	H. Rose.
Copper	Cu	31·7	Cupric oxide, Cu^2O	Erdmann and Marchand.
Didymium	Di	48	Oxide, Di^2O	Marignac.
Erbium	E			
Fluorine	F	19	Fluoride of calcium, CaF „ „ sodium, NaF	Louyet. Dumas.
Glucinum	Gl	4·7 7·0	Glucina, Gl^2O „ Gl^4O^3	Awdejew.
Gold	Au	196	Auric chloride, $AuCl^3$	Levol, Berzelius.
Hydrogen	H	1	Water, H^2O	Dumas; Erdmann and Marchand.
Iodine	I	127	Iodide of potassium, KI „ „ silver, AgI	Marignac. Dumas.
Iridium	Ir	98·6	Dichloride, $IrCl^2$	Berzelius.
Iron	Fe	28	Ferric oxide, Fe^4O^3 Ferric chloride, Fe^2Cl^3	Svanberg and Norlin. Maumené, Erdmann and Marchand. Berzelius. Dumas.
Lanthanum	La	46	Oxide, La^2O	Marignac.
Lead	Pb	103·6	„ Pb^2O	Berzelius.
Lithium	Li	6·5 7·0	„ Li^2O Carbonate, Li^2CO^3 Sulphate, Li^2SO^4	„ Troost. Mallet.
Magnesium	Mg	12	Magnesia, Mg^2O Chloride, MgCl	Berzelius. Dumas.
Manganese	Mn	27·6	„ MnCl	Berzelius.
Mercury	Hg	100	Mercuric oxide, Hg^2O	Erdmann and Marchand.
Molybdenum	Mo	46 48	Molybdic anhydride, Mo^2O^3	Svanberg and Struve; Berlin. Dumas.
Nickel	Ni	29 29·5	Oxide, Ni^2O Chloride, NiCl	Schneider. Dumas.
Nitrogen	N	14	Sal-ammoniac, NH^4Cl	Pelouze, Marignac, Penny.
Osmium	Os	100	Dichloride, $OsCl^2$	Berzelius, Frémy.
Oxygen	O	16		
Palladium	Pd	53	Chloride, PdCl	Berzelius.
Phosphorus	P	31	Phosphoric anhydride, P^2O^5 Pentachloride, PCl^5	Schrötter. Dumas.
Platinum	Pt	99	Dichloride, $PtCl^2$	Berzelius, Andrews.
Potassium	K	39 39·2	Chloride, KCl	Marignac, Frémy, Maumené. Stas.
Rhodium	Rh	52	Sesquichloride, Rh^2Cl^3	Berzelius.
Ruthenium	Ru	52	„ „ Ru^2Cl^3	Claus.
Selenium	Se	79	Selenide of mercury, Hg^2Se	Berzelius, Sacc, Erdmann and Marchand.
Silicon	Si	28	Chloride, $SiCl^4$	Dumas.
Silver	Ag	108	„ AgCl	Marignac, Maumené, Penny, Berzelius
Sodium	Na	23	„ NaCl	Penny, Pelouze, Dumas.
Strontium	Sr	43·8	„ SrCl	Dumas.
Sulphur	S	32	Cinnabar, Hg^2S Sulphide of silver, Ag^2S	Erdmann and Marchand, Struve. Dumas.
Tantalum	Ta	137·6	Tetrachloride, $TaCl^4$	H. Rose.
Tellurium	Te	128	Bromide of potassium and tellurium, K^2TeBr^6	v. Hauer.
Terbium	Tr			
Thorinum	Th	59·5	Thorina, Th^2O	Berzelius.
Tin	Sn	116 118	Stannic oxide, SnO^2 „ chloride, $SnCl^4$	Mulder, Vlaanderen. Dumas.
Titanium	Ti	50	Tetrachloride, $TiCl^4$	Pierre.
Tungsten	W	92	Tungstic anhydride, W^2O^3	Schneider, Birch, Dumas.
Uranium	U	60	Uranic oxide, U^4O^3	Péligot.
Vanadium	V	68·5	Vanadic anhydride, V^2O^3	Berzelius.
Yttrium	Y			
Zinc	Zn	32·5	Oxide, Zn^2O	A. Erdmann.
Zirconium	Zr	33·5 89·5	Zirconia, Zr^4O^3 „ ZrO^2	Berzelius, Erdmann.

We will now turn our attention to the determination of atomic weights from physical considerations, and observe how far the weights deduced from physical and chemical considerations coincide with one another. In the first place then, we will discuss the combining volumes of gases and vapours; from the observation of which we derive the most important of all means for controlling our conclusions as to the atomic weights of volatile bodies. If we take the specific gravity of hydrogen gas as unity, we find experimentally that the specific gravities of most other elementary gases and vapours are represented by the numbers we have selected to express their atomic weights. Hence, these atomic numbers represent the weights of equal volumes of the respective gases and vapours; and the formula of a compound body shows the number of elementary volumes of which it is composed. Thus while the formula for nitric acid HNO^3 represents a compound of one part of hydrogen, fourteen parts of nitrogen, and three times sixteen parts of oxygen, it also represents a compound of one volume of hydrogen, one of nitrogen, and three of oxygen. The relative specific gravities of the following elements, when in the gaseous state, and exposed to the same pressure and temperature, have been ascertained to be respectively:

$H = 1$ $Cl = 35{\cdot}5$ $O = 16$ $N = 14$
$Hg = 100$ $Br = 80$ $S = 32$ $P = \frac{31}{2}$
$Cd = 56$ $I = 127$ $Se = 79{\cdot}5$ $As = \frac{75}{2}$

Hydrochloric acid gas is composed of one volume of hydrogen, and one volume of chlorine united without any condensation. Consequently the molecule of hydrochloric acid is represented by two volumes of gas □□, whilst the atoms of hydrogen and chlorine respectively are represented by one volume only □. Hence while the specific gravity, or weight of a unit of volume of chlorine coincides with its atomic weight, the specific gravity or weight of a unit of volume of hydrochloric acid coincides with the half of its atomic weight, $\frac{1 + 35{\cdot}5}{2} = 18{\cdot}25$. Now ninety-nine per cent. of all known volatile compounds agree with hydrochloric acid in this particular, namely, that their specific gravities in the gaseous state are the halves of their atomic weights. Thus the atomic weight of water $H^2O^{1\times16}$, being 18, one volume of steam is found to be 9 times as heavy as one volume of hydrogen. The atomic weight of ammonia, $H^3N^{1\times14}$, being 17, one volume of ammoniacal gas is found to be 8·5 times as heavy as one volume of hydrogen. The atomic weight of marsh-gas, $H^4C^{1\times12}$, being 16, one volume of the gas is found to be 8 times as heavy as one volume of hydrogen, and so forth. Inasmuch, therefore, as half the atomic weight coincides with the specific gravity, or weight of one unit of volume, the entire atomic weight must represent *twice* the specific gravity or the weight of two units of volume; a conclusion which may be confirmed by actual experiment. Thus one volume of oxygen, and two volumes of hydrogen at the temperature 100° C. can be converted into two volumes of steam at the temperature 100°. Again two volumes of ammonia, when decomposed by the transmission of a series of electric sparks, yield one volume of nitrogen, and three volumes of hydrogen. No matter what the number of atoms or volumes which enter into the constitution of any volatile compound, they all become condensed into two volumes, as shown by the fact that the specific gravity or vapour-density of the compound is the half of its atomic weight.

Seeing that the molecule of a compound body corresponds with two volumes of gas or vapour, and the atom of an element with but one volume, it is evident that the quantity of an element which is strictly comparable to the molecule of a compound body must be represented by two atoms. Hence the symbols $\boxed{H \mid H}$, $\boxed{H \mid Cl}$, and $\boxed{Cl \mid Cl}$, represent comparable quantities of the three bodies, hydrogen, hydrochloric acid, and chlorine respectively which, thus formulated, present an obvious relation of sequence to one another. By the molecule of an element, therefore, we invariably understand two atoms or two volumes; and there is great reason to believe that our acquaintance with the uncombined elements pertains exclusively to their molecules. So that while Cl, for instance, represents the atom, or smallest proportion of chlorine that can enter into a combination, Cl^2 represents the molecule or smallest proportion of free chlorine that can result from or effect a reaction. There are certain compound molecular groupings also, which like the elementary molecules, occupy two volumes when in the free state, and become halved in combination. Thus ethyl in the free state is represented by C^4H^{10} = □□, in the combined state by C^2H^5 = □, and so in other instances.

It is evident from the preceding observations that, in the great majority of instances, the molecules we have deduced from chemical considerations, are identical with the molecules deduced from the physical law of gaseous volumes enunciated by Ampère, namely, that all gases contain the same number of molecules within the same volume. But if we had represented water by the formula $HO^{1\times8}$, sulphydric acid by the formula $HS^{1\times16}$, and carbonic oxide by the formula $C^{1\times6}O^{1\times8}$, we should have represented their molecules as having only half the volume of the molecule of hydrochloric acid, and should consequently have violated Ampère's physical law. The general conclusions at which we have arrived, however, namely that the chemical atoms of elementary bodies correspond with one gaseous volume, and the chemical molecules of simple or compound bodies, with two gaseous volumes, is quite in accordance with physical requirements. Nevertheless there are some exceptions, real or apparent, to which we must now direct our attention. We may premise by saying that some chemists attach so great an importance to the law of volumes, that they would be guided exclusively by it, and would accord to all bodies whatsoever, such atomic weights as would be in accordance with it. In the present state of knowledge, however, it seems to us preferable to deduce the chemical atom or molecule of a body chiefly from chemical considerations, and to wait for further investigation to clear up the few anomalies which at present exist between the results of chemical and physical inquiry.

Certain apparent exceptions to the law of volumes have of late years been satisfactorily explained away, by having regard to the following habitudes of volatile bodies. In the first place, some vapours, at temperatures but little raised above their condensing points, have anomalous densities which are much too high, or, in other words, the volumes of their atomic proportions are much too small; whereas at higher temperatures their densities and volumes are perfectly normal. Thus at a temperature a little above its condensing point, an atomic proportion of sulphur vapour occupies only $\frac{2}{3}$ the bulk of an atomic proportion of hydrogen gas at the same temperature; but at the temperature 1000° C. the two atomic proportions occupy the same volume. Again the molecule of acetic acid vapour at the temperature 230° C. has the same volume as the molecule of hydrochloric acid gas at that temperature; but at lower temperatures, its volume decreases almost to one-half that of hydrochloric acid gas at the same temperatures. In reference to this property it must be borne in mind that vapours near their condensing points manifest variations from several of the physical laws affecting gases. It would seem, indeed, that a vapour must be heated to a temperature considerably above its condensing point before it acquires the properties of a perfect gas. The recognition of this circumstance enables us to account in several instances for those departures from Ampère's law, in which the density of the gas is too high. In the second place, several compounds at the high temperatures required to bring them into a perfectly elastic state, seem to undergo a change, which has been investigated by Kopp, Marignac, Deville, Hofmann, Kékulé and others, and has been termed *disassociation*. According to these investigators, the molecule of a volatile compound, when strongly heated, sometimes breaks up into two simpler molecules which, on a reduction of temperature, reunite to form the original body, so that at the temperature at which the density is taken, we are really operating, not upon one more complex, but upon two less complex molecules; whence the densities are found to correspond with four volumes of vapour instead of with only two. The anomalous volumes or densities of the following compounds have been explained in this way.

	4 Vols		2 Vols.		2 Vols.
Sal-ammoniac	NH^4Cl	=	NH^3	+	HCl.
Sulphuric acid	H^2SO^4	=	SO^3	+	H^2O.
Pentachloride of phosphorus . .	PCl^5	=	PCl^3	+	Cl^2.
Hydrate of ethylendiamine . . .	$C^2H^{10}N^2O$	=	$C^2H^8N^2$	+	H^2O.

The phenomenon of disassociation then frequently enables us to explain various departures from Ampère's law, in which the densities are too low; or in which, in other words, the volumes are too great. But there still remain certain exceptions, which, in the present state of knowledge, cannot be satisfactorily explained by either of the above described considerations. Thus the atomic volumes of the vapours of phosphorus and arsenic respectively, are only one-half that of hydrogen. In order to make their atomic weights correspond with their atomic volumes, the ordinarily received atomic weights would have to be doubled, whereby they would become 62 and 150 respectively. But this doubling of the atomic weights of phosphorus and arsenic would be in violation of all chemical considerations, and likewise of all physical considerations except that relating to the atomic volumes of the elements themselves. Thus the formula for phosphamine would become $P^{1 \times 62}H^6$, and that for arsenamine $As^{1 \times 150}H^6$, despite the analogy of the two compounds to ammonia NH^3, and despite the fact that the hydrogen of the two compounds is divisible into thirds only and not into sixths. Moreover the vapour-densities of the compounds $P^{1 \times 62}H^6$ and $As^{1 \times 150}H^6$ would correspond to 4 volumes instead of 2, and would consequently be in opposition to Ampère's law. Again, the atomic heats of phosphorus and arsenic corresponding to the atomic weights 62 and 150 respectively, would be twice as high as the highest atomic heat of any other element. Lastly, by doubling the atomic weights of arsenic and phosphorus, the isomorphism of certain compounds of ammonia with the corresponding compounds of phosphamine and arsenamine would become unintelligible. At present then we are forced to admit that the vapour-densities of the elements, phosphorus and arsenic, are anomalous, and that we are incapable of explaining the cause of the anomaly. It may be that the vapours of these elements, like that of sulphur, though anomalous at one temperature, become normal at a higher temperature, though it must be admitted that the recent experiments of Deville do not countenance such an expectation. Or it may be that the anomalies depend upon allotropy. Phosphorus and arsenic are known to exist in different allotropic conditions, and it is not improbable that each allotropic form may have a different atomic weight. Hence the anomaly might be explained by supposing that phosphamine, for instance, contains the element phosphorosum, having the atomic weight 31; whilst phosphorus-vapour is composed of the element phosphoricum, having the atomic weight 62. This supposition of vapour-allotropy might also serve to explain the anomolous vapour-density of acetic acid at a low temperature. Normal acetate of potassium has the formula $C^2H^3KO^2$, but there is also an acid-acetate having the formula $C^4H^7KO^4$. The small vapour-density might possibly represent an acetic acid corresponding to the former salt, and the high vapour-density an acetic acid corresponding to the latter.

Certain other real or apparent exceptions to the law of volumes, are afforded by the chlorides and ethylides of zinc, mercury, and some other metals, as indicated below:

Hydrochloric acid	HCl	= 2 vols.		
Hydride of ethyl	HEt	,, ,,		
Chloride of ethyl	ClEt	,, ,,		
Chloride of mercury	HgCl	= 1 vol.	or Hg^2Cl^2	= 2 vols.
Ethylide of mercury	HgEt	,, ,,	,, Hg^2Et^2	,, ,,
Ethylide of zinc	ZnEt	,, ,,	,, Zn^2Et^2	,, ,,
Methylide of zinc	ZnMe	,, ,,	,, Zn^2Me^2	,, ,,

In consequence of the anomalous vapour-densities of the molecules of these compounds, as above expressed, some chemists have proposed to double the ordinarily received atomic weight of the metals mercury and zinc, so as to represent the molecules of the above volatile compounds by the following 2-volume formulæ; and it must be acknowledged that very strong reasons may be urged in favour of the duplication:

	Chloride of mercury	$Cl^2Hg^{1 \times 200}$
	Ethylide of mercury	$Et^2Hg^{1 \times 200}$
	Ethylide of zinc	$Et^2Zn^{1 \times 65}$
	Methylide of zinc	$Me^2Zn^{1 \times 65}$
corresponding to	Hypochlorous oxide	$Cl^2O^{1 \times 16}$
	Water	$H^2O^{1 \times 16}$

It is admitted both by those who advocate and those who deprecate the proposal, that the duplication of the atomic weights of the metals mercury and zinc, would necessitate the duplication of the atomic weights of several other metals, including magnesium, cadmium, lead, copper, iron, chromium, and aluminium. Now the principal objections to the adoption of this proposal are the following. Firstly, because, although the duplication of the atomic weights of the metals would bring the volumes of their chlorides and ethylides into accordance with Ampère's law, it would bring the volumes of the elements themselves into discordance therewith. Thus, the atomic volumes of mercury and cadmium corresponding to the atomic weights 200 and 112 respectively, would each be twice as great as the atomic volume of any other element. Secondly, because the chlorides, oxides, &c., of these metals, which are ordinarily represented as proto-compounds, would have to be represented as deuto-compounds, thus $HgCl^2$, $ZnCl^2$, $CdCl^2$, &c., a result not warranted by chemical considerations, seeing that in their chemical properties, these compounds are quite undistinguishable from undisputed proto-compounds. Moreover, the adoption of these doubled atomic weights would lead to most complex expressions for very many compounds. Of course, if it could be proved that the true atomic weights of these metals were really the doubles of those ordinarily employed, the circumstance of the duplication leading to inconvenient formulæ would have to be disregarded; but in the absence of such proof, the complexity to which the conclusion would lead is *pro tanto* evidence against the probability of its being true. Thus, phosphate of lead would become $Pb''^3P^2O^8$ instead of Pb^3PO^4; potassio-sulphate of copper would beecome $K^2Cu''(SO^4)^2.6H^2O$ instead of $KCuSO^4.3H^2O$; sulphovinate of zinc would become $Et^2Zn''(SO^4)^2.2H^2O$ instead of $EtZnSO^4.H^2O$; mercaptide of mercury would become $Et^2Hg''S^2$ instead of EtHgS, &c. &c.

Other exceptions to Ampère's law are furnished by the sesquichlorides of aluminium, iron, and chromium, the vapour densities of each of which, as determined by Deville, correspond to one volume of vapour only, instead of to two volumes. Hence it has been proposed to double the weights of the molecules of these compounds, and to represent them by the formulæ Al^4Cl^6, Fe^4Cl^6, and Cr^4Cl^6 respectively. But it is observable that if the molecule of sesquichloride of aluminium really contains 6 atoms of chlorine, it must also contain 55 parts of aluminium, and as a consequence, 55 parts of aluminium will constitute the smallest combining proportion of the metal, or the smallest, quantity which ever exists in a combination; in which case the smallest combining proportion of aluminium will have twice the specific heat of the smallest combining proportion of any other element, a result that must throw considerable doubt upon the propriety of the change on which it would be consequent. Again the vapour-density and chemical relations of chlorochromic aldehyde alike show that its molecule must be expressed by the formula $Cr^2O^2Cl^2$; while the correlations of sesquichloride of chromium and chlorochromic aldehyde require the molecules of the two compounds to be represented by formulæ expressing the same amount of chromium, which would not be the case if the sesquichloride were represented by the formula Cr^4Cl^6. There is, moreover, another compound, namely, arsenious anhydride, As^2O^3, the vapour-density of which corresponds to only one volume of vapour instead of two volumes, although no reason for the anomaly has yet been brought forward. There are also three well-known compounds, the vapour-densities of each of which correspond to four volumes, instead of to only two, namely, nitric oxide, N^2O^2, pernitric oxide, N^2O^4, and perchloric oxide, Cl^2O^4. In its chemical relations, the molecule of nitric oxide, N^2O^2, corresponds to the molecule of chlorine, Cl^2, and the atom of nitric oxide, NO, corresponds to the atom of chlorine, Cl: but whilst the atom of chlorine corresponds to one volume, and the molecule of chlorine to two volumes, the atom of nitric oxide corresponds to two volumes, and its molecule to four volumes of gas, and similarly with pernitric oxide and perchloric oxide. At present no satisfactory explanation has been given of these anomalies, though it is not improbable that they may be explicable on the principle of disassociation. Thus, it is possible that the atom of sulphurous anhydride, $(SO^2)''$, which, like that of oxygen, O'', is capable of displacing two atoms of hydrogen, would also, like the atom of oxygen, be represented by one gaseous volume, were it not for the circumstance that the molecule of oxygen, O^2, cannot split into two other molecules, whereas the molecule of sulphurous anhydride, S^2O^4, corresponding thereto in equivalency, can split into two separate molecules, each of which is capable of occupying two volumes; and this relation of oxygen to the diequivalent atoms of sulphurous anhydride, sulphuric anhydride, carbonic oxide, carbonic anhydride, &c., may be a parallel of the relation which subsists between chlorine and the protequivalent atoms of nitric oxide, pernitric oxide, and perchloric oxide respectively.

Out of many hundred volatile bodies whose vapour-densities have been ascertained, the following table comprises all the well-known exceptions to Ampère's law, though doubtless the strict chemical analogues of some of these bodies would also prove exceptional:

Symbol.	Vapour.	Atomic weight.	Theoretical volume.	Actual volume.
P	Phosphorus	P = 31	1	$\frac{1}{2}$
As	Arsenic	As = 75	1	$\frac{1}{2}$
HgCl	Corrosive sublimate	Hg = 100	2	1
HgEt	Mercuric ethyl		2	1
HgMe	Mercuric methyl		2	1
ZnEt	Zinc-ethyl	Zn = 32·5	2	1
ZnMe	Zinc-methyl		2	1
As^2O^3	Arsenious anhydride	As = 75	2	1
Al^2Cl^3	Aluminic chloride	Al = 13·75	2	1
Fe^2Cl^3	Ferric chloride	Fe = 28	2	1
$Cr Cl^3$	Chromic chloride	Cr = 26·2	2	1
N^2O^2	Nitric oxide	N = 14	2	4
N^2O^4	Pernitric oxide		2	4
Cl^2O^4	Perchloric oxide	Cl = 35·5	2	4
H^2SO^4	Sulphuric acid	S = 16	2	4
NH^4Cl	Sal-ammoniac	N = 14	2	4
NH^4CN	Cyanide of ammonium	C = 12	2	4
$NH^4.HS$	Sulphydrate of ammonium	S = 32	2	4
PCl^5	Pentachloride of phosphorus	P = 31	2	4
$C^2H^{10}N^2O$	Hydrate of ethylene-diammonium	C = 12	2	4
$C^6H^{18}N^2O$	Hydrate of diethyl-ethylene-diammonium		2	4

The anomalous volumes of the last seven compounds are clearly explicable on the principle of disassociation. With regard to the duplication of the atomic weights of those metals whose chlorides and ethylides have anomalous densities, it must be remembered that the proposal is at present young, and that further investigation may suffice to remove some of the objections which at present surround it; precisely as further investigation removed the objections which in the first instance seemed to oppose with overwhelming force, Gerhardt's proposal to double the then received atomic weights of carbon, oxygen, and sulphur. This same remark applies to the proposal of Cannizzaro, which we shall next have to consider.

It was contended by Dulong and Petit, who were the earliest investigators on the subject, that all elementary atoms have the same capacity for heat, or, in other words, that the specific heats of all elementary atoms are the same. If this law be admitted, it is obvious that the determination of the specific heat of an element must furnish a ready means of fixing its atomic weight. The atomic heats of simple and compound bodies have been of late years ascertained with great care, though from the nature of the subject it can scarcely be said with great accuracy, by Regnault, whose results, corresponding to the atoms which we have adopted, are as follows:—

12	Carbon	2·89	80	Bromine	6·74
32·5	Zinc	3·10	127	Iodine	6·87
56	Cadmium	3·16	32	Sulphur	6·48
13·75	Aluminium	2·93	79	Selenium	6·62
28	Iron	3·18	128	Tellurium	6·06
29·5	Nickel	3·20	31	Phosphorus	5·85
29·5	Cobalt	3·15	75	Arsenic	6·10
31·7	Copper	3·01	120·3	Antimony	6·09
100	Mercury	3·19	210	Bismuth	6·57
103·6	Lead	3·25	118	Tin	6·57
53	Palladium	3·15	23	Sodium	6·75
99	Platinum	3·19	39	Potassium	6·71
27·5	Manganese	3·1	108	Silver	6·16
26·2	Chromium		196	Gold	6·38
12	Magnesium				
20	Calcium				
43·8	Strontium				
68·6	Barium				

The numbers representing Regnault's atomic heats were obtained by multiplying the observed specific heats of the bodies, referred to that of water as unity, by their atomic weights on the oxygen scale. But it would be found more convenient in practice to assume the atomic heat of lead, which corresponds nearly with the mean atomic heat, as unity; whereby the atomic heats of the first class of metals would approximate more or less closely to the number 1, and those of the second class to the number 2. On this scale, the specific heats of the first class elements would correspond to the reciprocals of their atomic weights on either scale, and those of the second class to twice their reciprocals.

At the time of Regnault's researches, the atomic weights of all the elements in the second column, with the exception of sodium, potassium, and silver, were frequently expressed by the halves of the numbers we have adopted. Regnault proposed to halve the atomic weights of these three metals also, whereby the atomic heats of all the elements would be in accordance with Dulong and Petit's law, and would be expressed by numbers approximating more or less closely to 3·0 on the water-unity scale, or to 1·0 on the lead-unity scale. It is observable that in no case does the experimental atomic heat thus obtained differ from the mean atomic heat in the proportion of 1·1, or 0·9, to 1·0; whereas the extreme atomic weights differ from one another in the ratio of 1 to 9. Concerning this close correspondence in the atomic heats of the elements, Graham writes: "The law (of Dulong and Petit) would probably represent the results of observation in a perfectly rigorous manner, if the specific heat of each body could be taken at a determinate point of its thermometrical scale, and if the specific heat could be further disencumbered of all the foreign influences which modify the observation," such as the original state of hardness or softness of the body, its crystalline or amorphous condition, the heat absorbed to produce softening, and the heat absorbed to produce dilatation, &c. Recent chemical research, however, has rendered it impossible for chemists to halve the atomic weights of the elements in the second column, so as to make their atomic heats coincide with that of lead; and hence Cannizzaro has been led to advocate a transposition of Regnault's proposal, so as to maintain the integrity of Dulong and Petit's law, by doubling the atomic weights of the metals in the first column, whereby the atomic heats of all the elements, with the possible exception of carbon, would be expressed by numbers approaching more or less closely to 6.

Cannizzaro has also pointed out that if his atomic weights were adopted, the atomic heats of many compound bodies, when divided by the number of their constituent atoms, would give a number approximating more or less closely to 6, or in other words, the atomic heats of these bodies approximate to the sum of the atomic heats of their constituent elements. It is observable, however, that the latter mode of expressing the fact applies equally well, whether or not we double the atomic weights in the first column. Thus the atomic heat of chloride of silver approximates to 6 + 6 or 12, and that of chloride of lead to 6 + 3, or 9.

It is evident that the atomic weights proposed by Cannizzaro, from considerations of specific heat, frequently correspond with those which he and others have been led to from considerations of atomic volume; and their adoption is consequently liable to the objections which we have already taken.

Cannizzaro's proposal, moreover, would involve the dissassociation of silver from lead, and that of the metals of the alkalis from those of the alkaline earths. The chlorides of silver and potassium, for instance, would be represented as protochlorides by the formulæ $AgCl$ and KCl respectively, whilst those of lead and barium would be represented as dichlorides by the formulæ $PbCl^2$ and $BaCl^2$ respectively. Now the highly basic characters of the alkaline earth-metals, the strongly alkaline reactions of their dissolved hydrates, the perfect neutrality and great permanency of their salts, seem to demonstrate their analogy to undisputed protequivalent metals, such as potassium, rather than to undisputed di-equivalent metals, such as tin. Again, the large number of similar compounds to which silver and lead give origin, the close resemblance in chemical properties of their corresponding compounds, their very general paramorphism, and not unfrequent isomorphism, seems to forbid their representation by discordant formulæ. The two metals are soft, malleable, fusible, volatile, and isomorphous. The two chlorides are anhydrous and insoluble, or sparingly soluble; the two sulphates are anhydrous, insoluble and similiform; the two hydrates are sparingly soluble, forming alkaline solutions; the two sodium-double-chlorides, potassium-double-iodides, protosulphides, cuprosulphides, monobasic and tribasic sulphantimonites, are similar in their chemical, and isomorphous in their physical relations.

It seems to us that the objections to Cannizzaro's general proposition, are, in the present state of knowledge, too great to admit of its adoption; but still it is a question whether some of the metals comprised in the first column might not advantageously, receive the doubles of their ordinarily admitted atomic weights. With regard to the metals palladium and platinum, for instance, it is not by any means improbable that their real atomic weights may prove to be 106 and 198 respectively. With regard to aluminium, again, it is certain that, so far as our actual knowledge goes, the smallest indivisible proportion of aluminium that can exist in a combination is twice the proportion expressed by its ordinarily received atomic weight, or, in other words, it amounts to 27·5, instead of to only 13·75 parts. All chemists invariably represent the compounds of aluminium to contain 27·5 parts of aluminium, which is indeed its smallest combining proportion or chemical atom. Consequently, by employing the number 13·75 to express the atomic weight of aluminium, all aluminous compounds have to be represented as containing two inseparable atoms, or some multiple of two inseparable atoms of the metal, a result which is evidently unphilosophical. The chemical habitudes of the metal aluminium resemble the chemical habitudes of the metal bismuth, 27·5 parts of the former corresponding to 210 parts of the latter: and there is no greater chemical reason for halving the 27·5 parts of aluminium in order to represent its trichloride as a sesquichloride, than there is for halving the 210 parts of bismuth in order to represent its trichloride as a sesquichloride. Somewhat similar observations apply to the metals, iron, manganese, and chrome, when entering into the constitution of ferric, manganic, and chromic salts, respectively. Throughout all the decompositions and recompositions of ferric compounds, for instance, so long as they continue to be ferric compounds, we find 56 parts of iron constituting one indivisible combining proportion or chemical atom. We have two allotropic forms of the metal iron, one of which we call *ferrosum*, having the atomic weight 28, the atomic heat 3, and combining with 1 atom of chlorine, to form a protochloride; — the other, which we call *ferricum*, having the atomic weight 56, the atomic heat 6, and combining with 3 proportions of chlorine to form a trichloride; and similarly with *chromosum* and *chromicum*, *manganosum* and *manganicum*. The ferrous and ferric atoms have distinct chemical properties and form distinct series of compounds, which differ more from one another than do the salts of ferrosum from those of nickel and copper, or than do the salts of ferricum from those of aluminium and bismuth. So great, indeed, is the difference, that, had we been unacquainted with the methods of converting ferrous and ferric compounds into one another, we should never have suspected them to contain the same metal, or even similar metals. Now, that two different allotropic forms of the same element may have different atomic weights and different equivalent functions, seems to be no longer questionable. Brodie's reseaches on *graphon* have shown conclusively that compounds may be prepared which contain the graphitic modification of carbon, and are altogether dissimilar from compounds containing the ordinary form of carbon. In fact, ordinary carbon-compounds present a greater analogy to corresponding compounds of sulphur than they do to any of the known compounds of graphon, precisely as the salts of ferrosum resemble salts of nickel more closely than they do the salts of ferricum. The only circumstance wanting to complete the parallel is that not only carbon and graphon compounds, but isolated carbon and graphon are known to chemists; whereas, though ferrous and ferric compounds are well known, chemists have not yet recognised any form of iron distinct from ferrosum, unless indeed we make the by no means improbable assumption that iron in the passive state constitutes ferricum. The specific heats of carbon, graphon, and diamond correspond clearly with different atomic weights. Thus, if we accord to carbon the atomic weight 12, to graphon the atomic weight 18, and to diamond the atomic weight 24, the atomic heats of the three bodies, calculating from Regnault's results, will be 2·8980, 3·6324, and 3·5232 respectively, giving a mean of 3·3512. But it seems probable from chemical considerations that the atomic weight of graphon is not 18, but 36 (33 Brodie), in which case its atomic heat will be 7·2048, or exactly as much above the mean as that of phosphorus is below it.

Precisely as the double atoms of iron and aluminium in ferric and aluminic salts constitute indivisible proportions, so do the double atoms of copper and mercury in cuprous and mercurous compounds constitute indivisible proportions throughout all the decompositions and recompositions of their respective salts. So long as the metals remain in the state of *cuprosum* and *mercurosum*, so long do 63·5 parts of the former and 200 parts of the latter constitute their respective atomic weights or smallest indivisible combining proportions. Each metal would have for its atomic heat the number 6, and would combine with one atom of chlorine to form a protochloride, so that while the atoms of ferrosum and ferricum combine with the halogens, &c., in different proportions, or, in other words, have different degrees of equivalency, the atoms of mercurosum, and mercuricum though having different atomic weights and different atomic heats, combine each with the same proportion of halogen, or, in other words, have the same degree of equivalency; and similarly with cuprosum and cupricum (see EQUIVALENTS). A convenient mode of representing the atoms of ferricum, mercurosum, &c., consists in doubling one of the letters of the respective symbols used to express the atoms of ferrosum and mercuricum, &c., so as to indicate that the atoms of the former elements are twice as heavy as those of the latter. In a similar manner the atom of graphon might be represented by the symbol Ccc, to imply that it had three times the atomic weight of carbon. In this way we might arrange the following series of atoms:

Atomic heats = 3.			Atomic heats = 6.		
Carbon .	. C''''	12	Graphon .	. Gr or Ccc	36
			Aluminium	. All'''	27·5
Ferrosum	. Fe'	28	Ferricum	. Ffe'''	56
Manganosum	. Mn'	27·5	Manganicum	. Mm'''	55
Chromosum	. Cr'	26·25	Chromicum	. Ccr'''	52·5
Mercuricum	. Hg'	100	Mercurosum	. Hhg'	200
Cupricum	. Cu'	31·75	Cuprosum	. Ccu'	63·5

By thus recognising the quantities represented in the second column as distinct atoms, we obtain nearly all the advantages, with scarcely any of the disadvantages, which would accrue from Cannizzaro's proposal, and are enabled to account satisfactorily for the frequent isomorphism or parallelism of the double proportions of these elements, with the single proportions of other elements, as illustrated below:

$KClO^4$	with	$KMmO^4$	instead of	KMn^2O^4
K^2SO^4	,,	K^2MmO^4	,,	$K^2Mn^2O^4$
K^2SO^4	,,	K^2CcrO^4	,,	$K^2Cr^2O^4$
SO^3	,,	$CcrO^3$	,,	Cr^2O^3
SO^2Cl^2	,,	$CcrO^2Cl^2$	,,	$Cr^2O^2Cl^2$
Ag^2S	,,	Ccu^2S	,,	Cu^4S
Ag^3SbS^3	,,	$Pb^2CcuSbS^3$	,,	$Pb^2Cu^2SbS^3$
Pb^2S	,,	$PbCcuS$	,,	$PbCu^2S$

In addition to vapour-density and specific heat, isomorphism also furnishes a valuable aid in the determination of atomic weights. As a rule, the isomorphism of a comparatively unknown substance, with a substance of which the formula and atomic weight are well determined, warrants us in according to the less known body a formula and atomic weight corresponding to those of the better known body. Thus, the isomorphism of the stannic and titanic anhydrides, of the chromate and molybdate of lead, of the sulphate and selenate of sodium, assists us materially in our determination of the atomic weights of titanium, molybdenum, and selenium respectively, and of the formulæ of their respective compounds. But atomic weights deduced chiefly from isomorphous considerations, require to be received with very great caution, for the following reasons. We sometimes find obvious chemical analogies to exist in cases, where from dimorphism, or some other cause, the isomorphism is very imperfectly developed; and on the contrary, we sometimes have a marked isomorphism existing between bodies whose chemical correlations are very unsatisfactory. Thus, the isomorphism of potassium and sodium salts is not by any means striking. Nitrate of potassium, for instance, usually crystallises in right rhombic prisms, and nitrate of sodium in rhomboïds. It seems, however, that each salt can crystallise in both systems, and that while the ordinary form of nitrate of sodium corresponds with the rare form of nitrate of potassium, the ordinary form of nitrate of potassium corresponds with the rare form of nitrate of sodium. Again, the chemical analogies of similar lead and mercury compounds are extremely well marked, but isomorphism is manifested in a very few instances only. Indeed the isomorphous relations of lead and calcium are more decided than are the isomorphous relations of lead and mercury. Again, tellurium is heteromorphous with its chemical analogues, selenium and sulphur, and isomorphous with its chemical heterologues, arsenic and antimony. One might here refer for a moment to the well-known isomorphism of certain sulphides and arsenides. Thus, sulphide of nickel, Ni^2S, is isomorphous with the arsenide Ni^2As, and the antimonide Ni^2Sb. Marcasite, Fe^2S^2, is isomorphous with mispickel, Fe^2SAs; and common pyrites, Fe^2S^2, with cobalt-blende, Co^2SAs, and smaltine, Co^2As^2. From this isomorphism a general analogy in composition between arsenic and sulphur compounds, might possibly be inferred, were it not that such an inference would speedily be found incompatible with the results of chemical analysis. But if arsenic had been a rare and imperfectly known element, the isomorphism of marcasite and mispickel might not improbably have led to the association of its compounds with those of sulphur instead of with those of phosphorus.

Moreover, 2 atoms of one element are not unfrequently isomorphous with 1 atom of another. We have already given several examples of this phenomenon when referring to the isomorphism of sulphates with chromates, M^2SO^4 and $M^2Cr^2O^4$, of perchlorates with permanganates, $MClO^4$ and MMn^2O^4, and of salts of silver with salts of cuprosum, Ag^2S and Cu^4S; and we have shown how the anomaly could be readily explained away. Nevertheless it may be useful to point out definitely the kind of difficulty to which this sort of isomorphism might possibly give rise. At the present time, the ordinary salts of zinc, iron, lead, and silver, are alike thought to be protosalts. Now we find that copper forms two chlorides, two oxides, two sulphides, &c., in one set of which, the proportion of copper is twice as great as in the other. Which of these sets then comprises the protosalts? Judging from the isomorphous relations of cupric compounds with salts of iron and zinc, we should say that the cupric compounds were protocompounds, and that the atomic weight of copper was 31·7. Judging, on the other hand, from the isomorphous relations of cuprous compounds with salts of lead and silver, we should say that the cuprous compounds were the protocompounds, and that the atomic weight of copper was 63·4.

Lastly, we find that isomorphism sometimes subsists between compounds of a somewhat similar, but not of a strictly analogous chemical constitution. Thus, hæmatite, $(Fe^2)^{''''''}O^3$, is isomorphous with ilmenite, $Fe''Ti''''O^3$; and zircon, $Z''''SiO^4$, with wernerite, $(Al^2)^{''''''}Ca''SiO^4$. Again, nitrate of sodium, $NaNO^3$, calc-spar, Ca^2CO^3, and red-silver, Ag^3SbS^3, are isomorphous with one another; as are also nitrate of potassium, KNO^3, arragonite, Ca^2CO^3, and bournonite, $Pb^2CcuSbS^3$. Perchlorate of potassium, $KClO^4$, is isomorphous with sulphate of barium, Ba^2SO^4; and sulphate of iron, $Fe^2SO^4.7H^2O$, is paramorphous, if not isomorphous, with arsenate of sodium, $Na^2HAsO^4.7H^2O$. These illustrations are sufficient to show that the inferences deducible from isomorphism, unless supported by chemical or by some other physical evidence, must not be inconsiderately adopted as certain means for the determination of atomic weights and chemical formulæ. W. O.

ATRAMENTUM STONE. *Atramentenstein.* — A product of the partial oxidation of iron pyrites, consisting of a mixture of ferrous and ferric sulphates with free ferric oxide and a variable quantity of cupric sulphate and undecomposed pyrites. It is used in the manufacture of ink (*atramentum*).

ATRIPLEX. Many plants belonging to this genus are used for the extraction of soda. (Rochleder.)

ATRIPLEX VERRUCIFERA, a chenopodiaceous plant growing in the Kergis steppes, leaves 12·5 per cent. of ash containing 43·3 per cent. of soluble salts, viz. 7·2 per cent. sulphate of potassium, 4·8 sulphate of sodium, and 8 carbonate of sodium, 24·6 chloride of sodium, and 1·9 caustic soda. (Göbel.)

ATROPIC ACID. An organic acid stated by Richter (J. pr. Chem. xi. 33) to exist in belladonna, and to be obtained by treating the aqueous extract with alcoholic ammonia, evaporating the solution with potash, and decomposing the resulting potassium-salt with sulphuric acid. It is said to resemble benzoic acid in form and volatility; but its properties, and indeed its separate existence, have not been well made out.

ATROPINE, or **DATURINE.** $C^{17}H^{23}NO^3$, or $C^{34}H^{23}NO^6$.—This alkali, discovered in 1833, almost at the same time by Geiger and Hess (Ann. Ch. Pharm. vii. 269), and by Mein (*ibid.* vi. 67), exists in all parts of the deadly nightshade (*Atropa Belladonna*); it is also contained in the seeds of the thorn-apple (*Datura stramonium*). The alkaloïd has been analysed by Liebig (Ann. Ch. Pharm. vi. 66), and by Planta (*ibid.* lxxxiv. 245); the latter has also analysed many of its salts.

To extract it, the roots of the belladonna are treated with strong alcohol, and the extract left some hours in contact with caustic lime, then filtered, and supersaturated with sulphuric acid, the alcohol having been previously driven off by a gentle heat. A concentrated solution of carbonate of potassium is then added, and the liquid filtered as soon as it begins to show turbidity. The crystals of atropine, which separate after a while, are purified by repeated crystallisation from alcohol. Care must be taken not to apply too strong a heat, as the atropine is easily decomposed.—Rabourdin extracts the atropine by chloroform. Fresh belladonna taken at the period of flowering, is heated to 80° or 90° C. to coagulate the albumin. The clarified juice, when cold, is mixed with caustic potash and chloroform, in the proportion of 4 grms. potash and 30 grms. chloroform to a litre; and the whole is agitated for a minute and then left to settle. After half an hour, the chloroform charged with atropine separates in the form of a greenish oil, which after being washed, is distilled till all the chloroform passes over. The residue in the retort is extracted with a little water acidulated with sulphuric acid, which dissolves the atropine, leaving a green resinous matter behind. The acid solution is then treated with carbonate of potassium, and the precipitated atropine crystallised from alcohol.

Atropine crystallises in colourless silky needles united in tufts; by slow evaporation of its alcoholic solution, it is often obtained in the form of a translucent vitreous mass. It is but slightly soluble in water, but dissolves readily in alcohol, less in ether. It is strongly alkaline, and has a very bitter taste. It melts at 90°, and volatilises at 140° C., undergoing partial decomposition. It is highly poisonous, causing vertigo, headache, and even death; it also produces persistent dilatation of the pupil.

Chlorine acts but slowly on atropine, producing a yellowish liquid, which contains a considerable quantity of hydrochlorate of atropine. Tincture of *iodine* colours it brown. Hot *nitric acid* attacks it, with evolution of red fumes. *Chloric acid* dissolves it, but deposits it again unaltered, by spontaneous evaporation.

Atropine dissolves readily in *acids*, but the salts are difficult to crystallise. They are bitter, acrid, and poisonous; inodorous in the pure state. They are permanent in the air at ordinary temperatures, but become coloured even at the temperature of boiling water; most of them are soluble in water and alcohol, and insoluble in pure ether. *Potash*, *ammonia*, and their *carbonates*, precipitate atropine only from highly concentrated solutions of its salts; the precipitate dissolves readily in excess of the alkali. *Tannin* precipitates it only after addition of hydrochloric acid.

Acetate of atropine forms nacreous prisms grouped in stars: it is permanent and very soluble; after being several times dissolved, it loses a little of its acid. (Geiger.)

The *chloro-aurate*, $C^{17}H^{23}NO^3.HCl.AuCl^3$, is precipitated as a yellow powder, gradually becoming crystalline, when a strong solution of hydrochlorate of atropine is poured into a dilute solution of trichloride of gold; the liquid should be well shaken during the mixing, to prevent the agglutination of the precipitate. The *chloromercurate* is precipitated only from very concentrated solutions. The chloroplatinate is a pulverulent precipitate, which rapidly agglutinates: it is very soluble in hydrochloric acid. The *hydrochlorate* crystallises in tufts (Geiger); according to Planta, it is uncrystallisable. The *nitrate* forms a syrupy deliquescent mass. The *picrate* is a yellow pulverulent precipitate. The *sulphate* crystallises, according to Geiger, in delicate, colourless, nacreous needles, grouped in stars or tufts: it is very soluble. Planta did not succeed in crystallising it. The *tartrate* is a syrupy mass, which becomes moist in contact with the air.

The *valerate*, prepared by dissolving atropine in an equivalent quantity of valerianic acid diluted with 2 pts. of ether, and cooled to 0° C., then adding a further quantity of rectified ether (of 60° Cartier), equal to five times the weight of the atropine used, and leaving the solution to itself in a glass cylinder at 10° C., forms colourless transparent rhombic crystals, which refract light strongly. According to Callmann (J. pr. Chim. lxxvi. 69), they contain $C^{17}H^{23}NO^{3} + \frac{1}{2}H^2O.C^5H^{10}O^2$. They melt at 42° C., give off the greater part of their water at 100°, and at 120° begin to evolve vapours of valerianic acid. The salt prepared as above is perfectly soluble in water.

AUGITE. *Pyroxene.* (Gm. iii. 402; Handw. d. Chem. ii. 556.) — The name of a class of minerals distinguished: —1. By a certain form, belonging to the monoclinic or oblique prismatic system, being a prism of 87° with the base inclined at an angle of 74°; —and 2. By the general formula $SiM^2O^3 = M^2O.SiO^2$, or $3\mathit{MO}.2\mathfrak{S}\mathrm{i}\mathit{O}^3$,* where M consists for the most part of Mg and Ca, giving the formula $\begin{matrix}\mathrm{Ca}\\ \mathrm{Mg}\end{matrix}\mathrm{O.SiO^2}$, less frequently of Fe or Mn. Occasionally also 1Mg is replaced by 3H (polymeric isomorphism); and in the varieties called aluminous augites, 1 at. SiO^2 by 1 at. Al^4O^3 (or $2\mathfrak{S}\mathrm{i}\mathit{O}^3$ by $3\mathit{Al}^2\mathit{O}^3$).

Specific gravity 3·23 to 3·5. Hardness = 3 to 6. Lustre vitreous, inclining to resinous: in some varieties, pearly. Colour green, of various shades, verging on one side to white or greyish-white, and on the other to brown or black. Streak white to grey. Transparent to opaque. Fracture conchoïdal to uneven. Brittle.

The nature of the metals, whether calcium, magnesium, or iron, which enter into the composition of the mineral, produces considerable variations, not only of colour, lustre, transparency, and density, but also of crystallographical development, sometimes giving rise to differences in the magnitude of the angles in the primitive forms. These differences of character constitute the distinctions between the several species of augite, the principal of which are the following.

Common Augite, (M = Ca, Mg, Fe), the silica being sometimes also replaced by alumina. Black, greenish, or brownish-black crystalline masses, with cleavage parallel to the faces of a monoclinic prism of 87° and 93°. Specific gravity 3·33 to 3·36. The best developed crystals are found in basalt and other volcanic rocks. It occurs in the lavas of Etna and Vesuvius, in the volcanic Eifel, in the Bohemian Mittelgebirge, in the Fassathal, Iceland, and in numerous other localities. In some of these augites, the Mg is almost wholly replaced by iron and calcium. *Hudsonite* from North America, contains chiefly iron and scarcely any magnesium, a considerable portion of the silica in this mineral is also replaced by alumina (SiO^2 by Al^4O^3).

Pyroxene.—This name is sometimes used as synonymous with augite, to denote the entire family; but it is especially applied by some mineralogists to certain varieties of augite, having a green or dark green colour, viz. *Fassaite*, *Coccolite* (consisting of an aggregation of roundish crystalline grains), *Funkite*, *Baikalite*, &c. They are distinguished from common augite chiefly by containing a smaller amount of iron.

Diopside (white augite, Mussite).—Essentially a silicate of calcium and magnesium, $(CaMg)SiO^3$, some varieties, however, containing small quantities of iron, manganese, and even hydrogen (H^2 instead of Mg). Colour, white, greyish, or greenish-white, and light green. Occurs in very fine crystals, especially on the Mussa Alp in Piedmont.

Malacolite.—An augite rich in magnesium, also containing hydrogen, calcium and iron being only subordinate. The water which it contains renders it softer than the anhydrous augites. *Salite* and *Pyrgom* are related in chemical composition to malacolite on the one hand, and to pyroxene and diopside on the other.

Diallage and *Broncite* are, like malacolite, hydrated augites rich in magnesia, but having also the silica more or less replaced by alumina. In *hypersthene*, the iron predominates very strongly as protoxide. All these minerals, to which also the *augitic talcs* are related (see TALC), possess a laminated structure, arising from the peculiar facility with which they cleave in a particular plane.

Asbestoïdal augites, are hydrated calcio-magnesian augites of fibrous structure: some of them occur as paramorphoses. This is the case with *Traversellite*, a hydrated ferroso-magnesian augite from Traversella in Piedmont. To this sub-species appears also to belong a nearly pure ferrous augite, analysed by Grann. (Compt. rend. xxiv. 794.)

The following minerals also belong to the augite family: *Ægyrin*, probably a calcio-sodium augite; *Acmite* or *Achmite* (p. 36), in which silica is replaced by alumina; *Spodumene* in which $3M^2O$ are replaced by Al^4O^3; *Jeffersonite*, an augite containing zinc; *Rhodonite*, a nearly pure manganese augite.

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* $\mathfrak{S}\mathrm{i}\mathit{O}^3 = 21 + 3 \times 8$. $SiO^2 = 28 + 2 \times 16$.

The following are analyses of certain varieties of augite:

	Wackenroder.	Bonsdorff.	H. Rose.			Berzelius.
	a	*b*	*c*	*d*	*e*	*f*
Lime	24·74	24·76	23·57	24·34	23·47	20·00
Magnesia	18·22	18·55	16·49	18·00	11·49	4·50
Protoxide of manganese	0·18	0·32	0·42	2·00	0·61	3·00
Protoxide of iron	2·50	0·99	4·44	1·08	10·02	18·85
Silica	54·16	54·83	54·86	54·64	54·08	50·00
Alumina	0·20	0·28	0·21			
	100·00	99·73	99·99	100·66	99·67	96·35

a is diopside from Fassa; *b* from Fammare; *c*, salite from Sala; *d*, malacolite from Orrijerfor; *e* from Dalecarlia; *f* from Dagerö.

Crystals having the form, structure, and composition of augite may be obtained by exposing a mixture of 1 at. lime, 1 at. magnesia, and 2 at. silica (SiO^3) to the heat of a porcelain furnace, and leaving it to cool very slowly (Berthier, Ann. Ch. Phys. [2] xxiv. 376); similar crystals are likewise found among the slags of blast-furnaces (Nöggerath, J. pr. Chem. xx. 501.)

The augites are not completely decomposed by any acid except hydrofluoric acid Their behaviour before the blowpipe varies according to their constitution. Diopside yields a colourless nearly transparent glass; ferruginous augite, a dark-coloured glass. Augite dissolves readily in borax, but with difficulty in microscosmic salt, forming a skeleton of silica.

AUGUSTITE. Syn. with APATITE.

AURADE. The name given by Plisson to a body which separates from oil of neroli, on addition of alcohol, in white nacreous laminæ; it is probably the camphor or stearoptene of the oil, and appears to agree in composition with the camphor of rose-oil. It melts at 50° C., and on cooling solidifies to a waxy non-crystalline mass; in a close vessel it sublimes without decomposition. It is insoluble in water, dissolves in 10 pts. of boiling alcohol of 44° Bm.; soluble also in ether and in oil of turpentine. It is not attacked by acids. Fresh oil of neroli, which appears to be richer in this substance than the old oil, yields about 1 per cent. of it. (Handw. d. Chem. ii. 558.)

AURANTIN. Syn. of HESPERIDIN.

AURICHALCITE. (Aurum, *gold*, and χαλκος, *ore*.) A mineral occurring in transparent, verdigris-green, needle-shaped crystals at Loktewsk on the Altai Mountains. It appears to contain $2CO^3Cu^2.3ZnHO$. When reduced, it yields a gold-coloured alloy of copper and zinc.

AUROTELLURITE. See TELLURIUM, GRAPHIC.

AUTOMALITE. See SPINEL.

AUTUNITE. Lime-uranite. (See URANITE.)

AURUM MOSAICUM or **MUSIVUM.** The old name of disulphide of tin prepared in the dry way. (See TIN.)

AVENIN. A nitrogenous substance contained in oats, similar to, and most probably identical with, legumin.

AVENTURIN or **AVANTURIN.** A variety of quartz rock, which, when polished, exhibits a strong reflected light from innumerable points of its surface, proceeding partly from minute crystals of mica embedded in the mineral, partly from minute cracks and fissures. The most beautiful comes from Spain, but very fine specimens have also been found at Glen Fernat in Scotland. The most usual colour is brown or reddish-brown, enclosing golden-coloured spangles. The mineral is used as a gem, but is often replaced by the artificial aventurin-glass, which even excels it in beauty.

AVENTURIN GLASS, also called *gold-flux*. — A brownish-coloured glass interspersed with small spangles, which give it a peculiar shining appearance. This glass was formerly used in the arts and for ornaments, and its preparation was long kept secret by the manufacturers at Murano near Venice: it is now, however, prepared in other localities. The following are analyses of this glass: *a*, by Schnedermann and Wöhler; *b*, by Péligot; *c*, by Kersten.

	SiO^2	P^2O^5	Al^4O^3	Fe^4O^3	Fe^2O	Ca^2O	Mg^2O	K^2O	Na^2O	Cu	Sn	Pb
a	65·2	1·5	—	6·5	—	8·0	4·5	2·1	3·2	3·0	trace	—
b	67·7	—	trace	—	3·5	8·9	—	5·5	7·1	3·9	2·3	1·1
c	67·3	—	—	2·4	—	9·0	—	5·3	7·0	4·0	2·3	1·0

Gahn first observed that the spangled appearance of the glass is due to minute shining, opaque, crystals, having the form of octahedral segments. Hence, and from the composition of the glass, it was concluded that the crystals consist of metallic copper. Clemandot and Fremy (Compt. rend. xii. 339), by melting together for 12 hours a mixture of 300 pts. of pounded glass, 40 pts. of copper filings, and 80 pts. of iron filings, and cooling slowly, obtained a rather dull-looking glass containing copper diffused through it in octahedral crystals.—Pettenkofer, on the other hand, maintains that the spangles consist of crystals of a cuprous silicate, identical in composition, but larger in size than the crystals of the compound which impart the deep-red colour to hæmatinone-glass or *porporino* (*q. v.*), and are diffused through a mass of glass coloured green by protoxide of iron, the red crystals seen through the green glass producing a mixed or resultant tint of brown. Aventurin-glass may in fact be prepared with certainty by adding to 100 pts. of a not too refractory glass, 8 to 10 pts. of a mixture of equal parts of ferrous and cuprous oxides, and leaving the mixture to cool very slowly so as to facilitate the formation of crystals. A red crystalline cuprous compound then separates, and the ferrous oxide remains in the glass, imparting a green colour. Pettenkofer has also converted hæmatinone into aventurin-glass by addition of iron. (Handw. d. Chem. 2ᵗᵉ Aufl. ii. 504.)

AVENTURIN GLAZE. A glazing for porcelain invented by Wöhler (Ann. Ch. Pharm. lxx. 57). To prepare it, 31 pts. of kaolin from Halle, 43 quartz-sand, 14 gypsum, and 12 porcelain fragments, the whole finely ground and levigated, are stirred up with 300 pts. of water, and to the paste thus formed are successively added the solutions of 19 pts. of acid chromate of potassium, 47 acetate of lead, 100 protosulphate of iron, and sufficient ammonia to precipitate the whole of the iron. After the potassium and ammonium-salts have been washed out by repeated decantation, the glazing is ready for use, and is laid on the burnt wares in the ordinary manner, and burnt by the heat of the porcelain furnace. When cold, it forms a brownish ground, containing crystalline laminæ which have a golden lustre, but appear green and transparent under the microscope and by transmitted light; these crystals are regarded by Wächter as chromic oxide or a compound of that oxide with ferric oxide.

AVIGNON, GRAINS OF. (*French Berries.*) See YELLOW-BERRIES.

AXE-STONE. A sub-species of jade, from which it differs in not being of so light a green, and in having a somewhat slaty texture. The natives of New Zealand work it into hatchets. It is found in Corsica, Switzerland, Saxony, and on the banks of the River Amazon, whence it has been called Amazonian stone. Its constituents are, silica 50·5, magnesia 31, alumina 10, oxide of iron 5·5, water 2·75, oxide of chromium 0·05. U.

AXINITE. A silicate containing boric acid, so named from the axe-like bevelling of its lateral edges. It is also called *Thumite*, from one of its localities, Thum in Saxony. Its formula is $6M^2O.2M^4O^3.8SiO^2.B^2O^3$, where M^2O stands for magnesia and protoxide of iron, and M^4O^3 for alumina, sesquioxide of iron, and sesquioxide of manganese (Gm. iii. 453). Crystalline system, the triclinic or doubly oblique prismatic. Specific gravity 3·294. Harder than felspar. Colour varying from a fine violet-brown to leek-green, sometimes plum-colour; some crystals are white and transparent, with a glassy lustre. Before the blowpipe it exhibits the reaction of boron with acid sulphate of potassium. In the unignited state, it is not attacked by hydrochloric acid, but yields to it after fusion. It is found in various localities in France, Norway, Saxony, the Harz, and the Alps; at Botallack, near the Land's End, Cornwall; and at Trewelland in that neighbourhood.

AZADIRINE. A bitter principle, perhaps an alkaloid extracted from *Melia Azadirachta*, an East Indian tree, by Piddington (Geiger's Mag. xix. 50), who states that it may be used as a substitute for quinine. According to O'Shaughnessy (Pharm. Centr. 1844, p. 365), all the parts of *Azadirachta Indica* are very bitter. The leaf is bitter and nauseating; the bark is peculiarly bitter, and somewhat astringent, and is used effectively in Bombay as a substitute for cinchona bark; the husk of the ripe fruit yields a very bitter fat oil, which possesses anthelmintic properties, and is used as an embrocation.

AZELAIC ACID. An acid stated by Laurent (Ann. Ch. Phys. [2] lxvi. 154) to be produced, together with suberic and other acids, in the oxidation of oleic acid by nitric acid. It closely resembles suberic acid, being distinguished merely by a lower melting point and greater solubility in ether. Laurent assigned to it the formula $C^{10}H^{18}O^4$; but it is probably nothing but impure suberic acid. (Compare Ann. Ch. Pharm. xxxv 103.)

AZOBENZENE. *Azobenzide*, *Azobenzol.* $C^{12}H^{10}N^2$. (Mitscherlich, Ann. Ch. Phys. xxxii. 224); Zinin, J. pr. Chem. xxxvi. 96; lvii. 173; Laurent and Gerhardt, Compt. chim. 1849, 417.)—A product of the reduction of nitrobenzene, or of the oxidation of benzidine. It is obtained, together with phenylamine, by the dry distillation of azoxybenzene; or simply by distilling a mixture of nitrobenzene and alcoholic potash; or by distilling a mixture of 1 pt. nitrobenzene, 3 pts. iron, and 1 pt. acetic acid (Noble). Azobenzene passes over towards the end of the operation, as a red oil, which solidifies on cooling; it is freed from aniline by hydrochloric acid, and recrystallised from alcohol or ether. It forms large reddish-yellow scales, scarcely soluble in water, readily in alcohol or ether. It melts at 65° C., boils* at 293°, and distils undecomposed (P. W. Hofmann). Vapour-density, by experiment, = 94, referred to hydrogen; 6·50 referred to air; by calculation (2 vol.), 91 referred to hydrogen, 6·32 referred to air (P. W. Hofmann, Ann. Ch. Pharm. cxv. 364). It is soluble in nitric or sulphuric acid, and is reprecipitated by water. Sulphide of ammonium and sulphurous acid convert it into benzidine. It is not decomposed when heated to 250° C. over soda-lime.

When acted on by fuming nitric acid, it yields two nitro-substitution compounds.—*Nitrazobenzene*, $C^{12}H^9(NO^2)N^2$, is formed when the reaction is not prolonged: it separates out in reddish-yellow crystals, which, after the acid has been decanted, are washed with water, and dissolved in boiling alcohol (which generally leaves a residue of the dinitro compound). The solution deposits orange-yellow crystals of nitrazobenzene, which are washed with alcohol and ether. When heated, it melts, and cools into a crystalline mass. It is less soluble in alcohol than azobenzene.—*Dinitrazobenzene*, $C^{12}H^8(NO^2)^2N^2$, is formed when the action of the nitric acid is prolonged for a few minutes: red crystals are deposited, which are washed with nitric acid, water, and ether, and recrystallised from boiling alcohol. It forms small reddish needles, which may be obtained larger by crystallisation from fuming nitric acid. When heated, it melts to a blood-red liquid, which crystallises on cooling. It is less soluble than nitrazobenzene in alcohol or ether. Sulphide of ammonium converts it into diphenine (*q. v.*) F. T. C.

AZOBENZIL. $C^{21}H^{15}NO$.(?) (Zinin, Ann. Ch. Pharm. xxxiv. 190; Laurent, Rev. scient. xix. 445).—Formed as a white granular precipitate, when a not too concentrated alcoholic solution of benzil is mixed with aqueous ammonia: after standing in the liquid for ten hours, it is washed and recrystallised from alcohol. It forms long, lustrous, iridescent needles, which are soluble in alcohol, alcoholic potash or ammonia, and hydrochloric acid (whence it crystallises unaltered); insoluble in water, potash, or ammonia. F. T. C.

AZOBENZOIDE. $C^{42}H^{32}N^3$ (?) (Laurent, Ann. Ch. Phys. [2] lxvi. 190).—A white amorphous powder, formed by the prolonged action of ammonia on crude bitter-almond oil. It is insoluble in alcohol and ether. When heated, it melts, and solidifies in crystalline granules; more strongly heated, it is decomposed.

F. T. C.

AZOBENZOIDINE. $C^{42}H^{27}N^3$. (?) (Laurent, Ann. Ch. Phys. [3] i. 302.)—A product of the action of ammonia on crude bitter-almond oil. It forms small, shining, oblique prisms: is inodorous, nearly insoluble in alcohol, slightly soluble in ether. It is dissolved and decomposed by nitric, hydrochloric, or sulphuric acid. It solidifies after fusion into a non-crystalline transparent mass. F. T. C.

AZOBENZOILIDE. $C^{14}H^{11}N$. (Laurent, Ann. Ch. Phys. [3] i. 304; xviii. 272.)—A product of the action of ammonia on pure bitter-almond oil. The oil was shaken up with potash and chloride of iron, distilled, and the first $\frac{1}{8}$ which passed over was covered with an equal volume of ammonia. Crystals were gradually deposited, and in three weeks the oil was half solidified. The mass, when extracted with ether, left a residue of azobenzoilide.

$$2(C^7H^6O) + NH^3 = C^{14}H^{11}N + 2H^2O.$$

It forms a microscopic crystalline powder, inodorous, insoluble in alcohol, very slightly soluble in ether. It is decomposed by prolonged fusion. Hot nitric acid dissolves it, apparently without decomposition; hot sulphuric acid dissolves it, forming a yellow solution, in which ammonia produces a white precipitate. F. T. C.

AZOBENZOYL. $C^{21}H^{16}N^2$. (Laurent, Ann. Ch. Phys. [2] lxvi. 185.)—A product of the action of ammonia on crude bitter-almond oil. When the yellow resinous mass obtained by leaving the oil for four weeks in contact with an equal volume of ammonia, is treated with boiling ether, a mixture of azobenzoyl and benzoylazotide is left undissolved: the former is dissolved out by boiling alcohol, and purified by recrystallisation. It forms a white, shining, crystalline, indorous powder, composed of irregular six-sided tables; insoluble in water, not very soluble in boiling alcohol. After fusion, it cools to a transparent mass; it is decomposed by a strong heat, leaving a residue of carbon.

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* The boiling point of azobenzene is commonly stated, on Mitscherlich's authority, to be 193° C. doubtless from a misprint in the original memoir.

According to Laurent (Ann. Ch. Phys. [3] i. 300), a mixture of equal volumes crude bitter-almond oil, ammonia, and sulphide of ammonium, solidifies after a long time; and on treating the product with boiling ether, a white crystalline powder remains behind, consisting of microscopic rhombic tables, which are nearly insoluble in alcohol, and slightly soluble in boiling ether. Laurent calls this body *hydrosulphate of azobenzoyl*, and assigns to it the formula $C^{21}H^{18}N^{2}S^{14}$, upon which no reliance can be placed. F. T. C.

AZOBENZOYL, HYDRIDE OF. Syn. with Hydrobenzamide (*q.v.*)

AZOCINNAMYL, HYDRIDE OF. See Cinnamyl.

AZOCODEINE. An organic base which Anderson obtained by the action of sulphide of ammonium on nitrocodeine. (See Codeine.)

AZODIFUNE. Gmelin's name for Azobenzide.

AZOERYTHRIN. See Orcein.

AZOLEIC ACID. Syn. with Œnanthylic Acid.

AZOLITHOFELLIC ACID. See Lithofellic Acid.

AZOLITMIN. See Litmus.

AZOMARIC ACID. See Pimaric Acid.

AZOPHENYLAMINE of Zinin. A product of the decomposition of nitrophenylamine by sulphide of ammonium. (See Phenylamine.)

AZOPHENYLAMINE of Gottlieb, more correctly *Nitrazophenylamine.* A product of the decomposition of dinitrophenylamine by sulphide of ammonium. (See Phenylamine.)

AZORITE. A mineral occurring in the trachytic rock of the Azore Islands, in small greenish or yellowish white pyramids. According to Hayes, it consists for the most part of tantalate of calcium.

AZOSULPHIDE OF BENZENE. Syn. with Hydride of Sulphazo-benzoyl or Thiobenzaldin. (See Benzoyl-hydride, decompositions by sulphide of ammonium.)

AZOTE. (α privative and ζωή life.)—Lavoisier's name for nitrogen.

AZOTAN. A name, not much used, for chloride of nitrogen.

AZOTIDES Syn. of Nitrides.

AZOXYBENZENE. *Azoxybenzide, Azoxybenzol.* $C^{12}H^{10}N^{2}O$. (Zinin, J. pr. Chem. xxxvi. 96; lvii. 173; further, Ann. Ch. Pharm. cxiv. 217; Laurent and Gerhardt, Compt. chim. 1849, 417.)—When to a solution of 1 pt. nitrobenzene in 10 vols. absolute alcohol, 1 pt. powdered potash is added, the whole becomes brown, and is heated to boiling. The mixture is shaken up and kept boiling for some minutes: on cooling it sometimes deposits brown crystals. The mother-liquor is decanted, and distilled till it forms two layers. The upper is a brown oily liquid, which, after decantation and washing with water, solidifies into a mass of brown needles; the lower contains aqueous potash, carbonate of potassium, and a brown potassic salt, almost insoluble in alcohol. The crystals are dried with filter-paper, and recrystallised from alcohol or ether: they are easily decolorised by passing chlorine through their alcoholic solution. 2 pts. nitrobenzene yield 1½ pt. azoxybenzene.

Thus obtained, azoxybenzene forms yellow, shining, four-sided needles, often an inch long, as hard as sugar, without smell or taste, insoluble in water, hydrochloric, or dilute sulphuric acid, potash, or ammonia, readily soluble in alcohol, still more so in ether. It melts at 36° C., and solidifies on cooling to a crystalline mass: it is decomposed by dry distillation, yielding aniline and azobenzene, and leaving a residue of carbon. It is not attacked by chlorine: bromine attacks it, forming a yellow componnd, very slightly soluble in alcohol. Strong sulphuric acid dissolves it, forming apparently a copulated acid. Sulphide of ammonium and sulphurous acid convert it into azobenzene.

Nitrazoxybenzene, $C^{12}H^{9}(NO^{2})N^{2}O$.—Azoxybenzene is not attacked by dilute nitric acid, but when gently heated with nitric acid of specific gravity 1·45, it dissolves, with great evolution of heat, and the liquid, if carefully cooled, solidifies after a while, to a thick pulp, consisting of two isomeric nitro-compounds, nitrazoxybenzene, and isonitrazoxybenzene, which may be separated by their different solubility in alcohol. If the pulp just mentioned be thrown on a filter, washed with water, treated three or four times with a quantity of boiling alcohol not sufficient to dissolve the whole (not more than 4 pts. alcohol to 1 pt. azoxybenzene), and the decanted liquors left to cool, crystals of nitrazoxybenzene are first deposited; and after a while, shining needles make their appearance in the midst of them. If the liquid be then filtered, and part of the alcohol distilled off, isonitrazozybenzene separates on cooling, in the form of an oil, which quickly solidifies in a crystalline mass; it may be purified by two or three crystallisations from small quantities of very strong alcohol.

Nitrazoxybenzene is a yellowish crystalline body, slightly soluble in boiling alcohol or ether. It is promptly attacked by boiling alcoholic potash, and coloured brown; on adding water, a yellowish-red powder is precipitated, which may be crystallised from boiling oil of turpentine. This compound appears to contain $C^{12}H^{9}N^{3}O$ (Laurent and Gerhardt). If the action of alcoholic potash be prolonged, the mixture becomes blue; the colour is destroyed by water. An alcoholic solution of sulphydrate of ammonium converts nitrazoxybenzene, with separation of 3 at. sulphur into a crystallisable base, which dissolves readily in alcohol and in benzene, and forms salts with acids.

Isonitrazoxybenzene forms crystals very much like those of nitrazoxybenzene, but easily soluble in alcohol. It dissolves also in a large quantity of ether, and in benzene, and often crystallises from these liquids in fine rhomboïdal prisms. It melts at 49° C. but does not volatilise without decomposition. When 1 pt. of this substance is treated with a solution of 1 pt. of potash in 8 pts. of alcohol, it melts and dissolves with ebullition, giving off the odour which is evolved on treating nitrobenzene with alcoholic potash. On boiling the liquid, a resinous mass separates, which yields by distillation an orange-coloured product, which crystallises from alcohol, and resembles nitrophenylamine. At the same time, an oily body is formed not possessing basic properties, and charcoal remains behind.

Isonitrazoxybenzene treated with alcoholic sulphydrate of ammonium, yields a body having the composition $C^{12}H^{9}N^{3}O$:

$$C^{12}H^{9}(NO^{2})N^{2}O + 2H^{2}S = C^{12}H^{9}N^{3}O + 2H^{2}O + S^{2}.$$

This body is insoluble in water, very soluble in alcohol, ether, benzene, and rock-oil soluble also in acids; but does not form definite salts. It melts at 85° C. to a yellow liquid, which solidifies on cooling, provided the temperatnre has not been raised too high. If a strong heat be applied, a brown liquid distils over, soluble in alcohol, though less so than the original substance. F. T. C.

AZOXYDIFUNE. Gmelin's name for Azoxybenzene.

AZULMIC ACID. A brown substance produced by the spontaneous decomposition of cyanogen and hydrocyanic acid.—An aqueous or a dilute alcoholic solution of cyanogen or aqueous hydrocyanic acid, when left to itself for some time, especially after addition of ammonia or potash, acquires a brown colour and gradually deposits brown flakes, consisting of azulmic acid. The solution contains azulmate of potassium or ammonium, from which the acid may be precipitated by the stronger acids. The same product is obtained by passing cyanogen gas into aqueous ammonia or alcoholic potash.—Respecting the composition of this substance, statements vary greatly; according to Pelouze and Richardson (Ann. Ch. Pharm. xxvi. 63), it is $C^{4}H^{4}N^{4}O^{2}$, that is to say, 4 at. cyanogen + $2H^{2}O$: but it is doubtful whether any of the analyses have been made upon a pure definite compound. The acid yields by dry distillation hydrocyanic acid, ammonia, and water, and leaves a residue of charcoal containing nitrogen. (For a full account of all the modes of preparation, properties, and reactions of azulmic acid, see Gmelin's Handbook, xi. 375.)

AZURE-BLUE. See Smalt.

AZURE-STONE } See Lazulite.
AZURITE }

B

BABINGTONITE. A mineral consisting principally of silicate of iron and calcium, found near Arendal in Norway, in the Shetland Isles, at Gouverneur in St. Lawrence County, New York, and at Athol in Massachusetts. It forms short, nearly right angled rhomboïdal prisms, of the triclinic system, with truncated edges and obtusely bevelled summits. Fracture imperfectly conchoïdal. Colour dark greenish-black, with vitreous lustre. Opaque in the mass, translucent in thin splinters. Hardness 5·5 to 6·0. Specific gravity 3·4 to 3·5. Brittle, producing a greenish-grey streak. Melts easily with intumescence before the blowpipe, forming a brownish-black shining globule, attracted by the magnet. It is slowly decomposed by boiling hydrochloric acid. The mineral has been analysed by Arppe (Berz. Jahresb. xxii. 20), and by R. D. Thomson (Phil. Mag. [3] xxvii. 123), but its formula has not yet been determined:

SiO^{2}	$Mg^{2}O$	$Ca^{2}O$	$Fe^{2}O$	$Mn^{2}O$	$Al^{4}O^{3}$	Loss by ignition.		
54·4	2·2	19·6	21·3	1·8	0·3	0·9	=	100·5 (Arppe)
47·5	2·2	14·7	16·8	10·2	6·5	1·2	=	99·1 (Thomson)

BABLAH or **NEB-NEB.** The commercial names for the fruits of several species of acacia. The principal varieties are East Indian bablah, from the *Acacia Bambolah* (*Roxburgh*), and Senegal and Egyptian bablah, from *Acacia nilotica* (*Delile*). The pericarp of these fruits contains a dark brown astringent juice. The aqueous extract contains, according to Chevreul (*Leçons de Chimie appliquée à la Teinture*, ii. 211), gallic and tannic acids, a red colouring matter, and a nitrogenous substance, besides other substances not yet examined. East Indian bablah yields to boiling water 49 per cent. of soluble matter; Senegal bablah 57 per cent.; nevertheless, according to Guibourt, the East Indian variety is richer in tannic and gallic acid, and therefore more valuable. Bablah is used in calico-printing in combination with alumina and iron mordants, to produce various shades of fawn-colour. The tint produced by the seeds is different from that obtained with the husks; the seeds are said to contain a red colouring matter, and to be used in Egypt and India for dyeing morocco. (Handw. d. Chem. 2te Aufl. ii. 603.)

BABUL-GUM or **GOND-BABUL**, an inferior sort of gum arabic, from the babul tree, *Acacia Arabica* (*Willd.*) growing in Bengal.

BABYLONIAN QUARTZ. This name is given to peculiar groups of quartz-crystals, composed of thin crystalline plates, disposed one above the other like terraces. It is found at Beerlston in Devonshire.

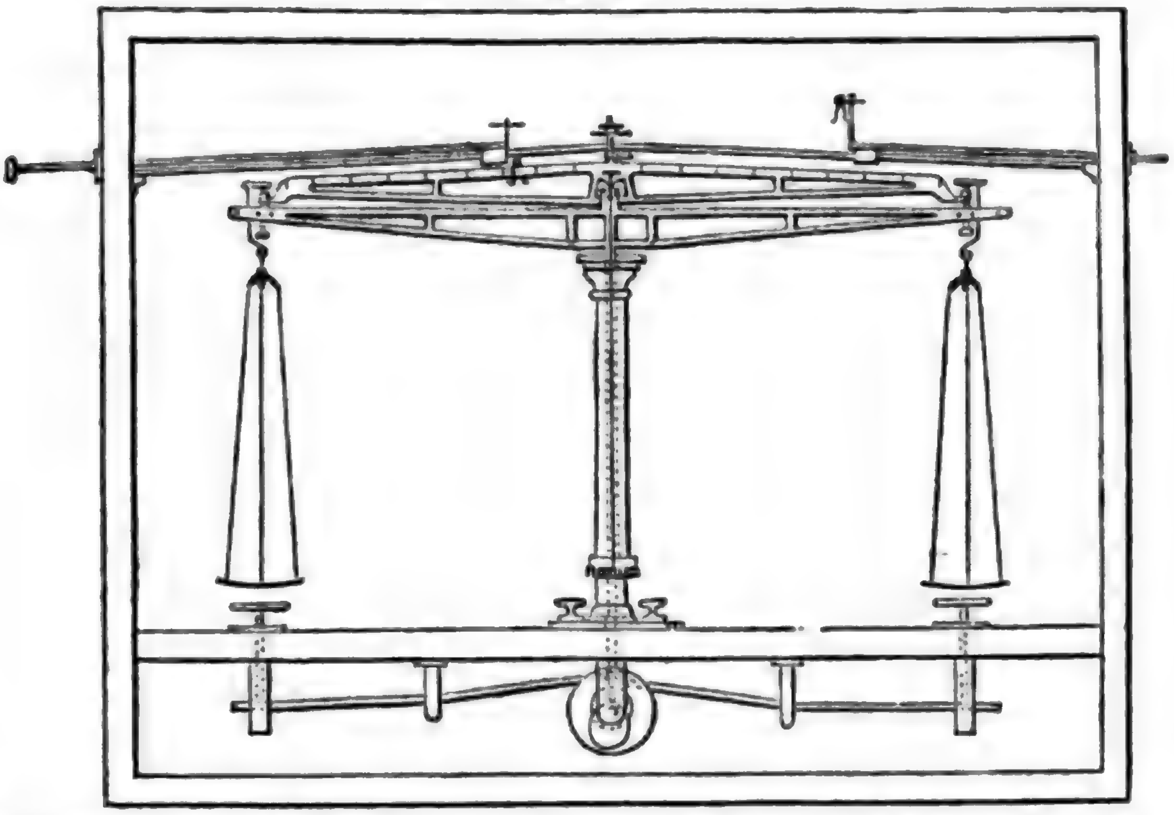
BAGRATIONITE. See Orthite.

BAIERIN or **BAIERITE.** A variety of niobite found at Bodenmais in Bavaria and at Limoges in France.

BAIKALITE. A green modification of diopside.

BALANCE. Chemistry being concerned with the relative masses or quantities of the elements which compose all known substances, and the weight or force of gravitation of a body being the only practicable measure of its mass or quantity of matter, the balance, which shows the equality of two weights, and may hence determine the ratio of all commensurable weights, is the chemist's most important instrument.

Fig. 78.

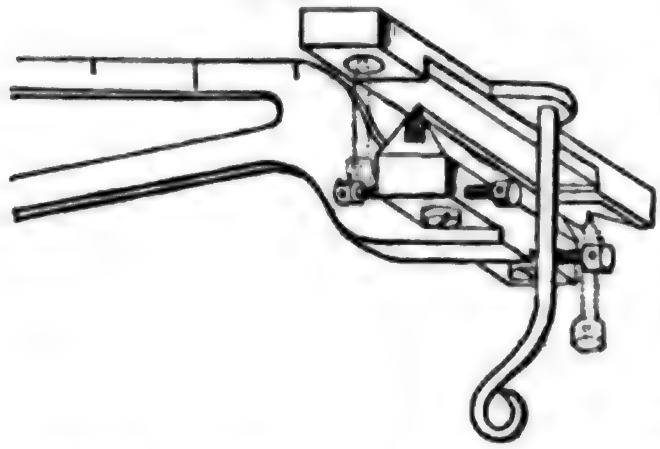


Theoretically speaking, the balance consists of a lever or inflexible straight line turning with perfect freedom on its central point. A weight is applied to each extreme point, and the force of gravity acting perpendicularly downwards, if either of these weights be in the least degree greater than the other, it will prevail and cause the lever to revolve in its own direction. The equilibrium of the lever or balance affords the desired criterion of perfect equality of weight; and an arbitrary weight being assumed as a standard, we can arrive, theoretically speaking, at any of its multiples or submultiples by successive duplication and bisection combined with addition and subtraction, and a perfect measure of all weights from the greatest to the least may thus be attained. The results of course are not absolute weights, as we say in common speech, but *ratios* of weights to each other, or to the standard unit-weight.

Practically, however, the balance consists of a metal beam with two almost equal and similar arms, suspended near its centre of gravity on a pivot, the weights to be compared being also suspended from two pivots at nearly equal distances from the centre pivot. In the balance thus constructed, we have by no means the simple and perfect comparison of two weights supposed in theory; the weight of the beam, the friction of the pivots, their unequal distances from the middle one, the resistance of the air, and possibly other causes, introduce small extraneous forces, which render the comparison required more or less uncertain and erroneous.

The Chemical Balance, is adapted for the ordinary operations of quantitative analysis, and is usually capable of weighing any quantity less than 100 grammes or 1500 grains. In its most perfect form (see *fig.* 78) it consists of a perforated brass beam, cast in a single piece, combining great strength and perfect inflexibility with comparatively small weight. It is suspended at the centre on a knife-edge of agate about an inch long, and turns on a single polished plane of agate fixed on a projecting brass support, which enters a perforation of the beam, and does not impede its motion. The agate knife-edge is firmly embedded in a wedge-shaped piece of brass, and being once adjusted exactly at right-angles to the plane of the beam, is then permanently fixed. At each end of the beam is a smaller agate prism (see *fig.* 79), with the edge uppermost, fixed in a brass setting, which is capable of a little lateral movement, but slides upon a brass plane, in such a manner that the two extreme edges and the centre edge are all appreciably in one plane, as may be seen by looking along them. The extreme edges may be moved to or from the centre edge by little adjusting screws, and fixed in the desired position with the assistance of two clamping screws.

Fig. 79.



Upon these extreme edges (*i. e.* knife-edges) are balanced two agate planes, from which, by the bent wire and a series of hooks and light wires, the pans are suspended.

Except, however, when a weighing is actually being made, the agate planes and edges are never in contact, but the beam and pan suspensions are borne by a frame or movement, having in the centre two Y's (*fig.* 78) which catch projecting pins close to the centre edge, and lift the beam about $\frac{1}{100}$ of an inch off the plane, while steel points (shown in dotted outline in *fig.* 79.) entering hollows in the lower surface of the pan-suspensions, likewise raise these planes off the edges, and retain them in the exact positions proper for a new experiment. The movement of the brass frame is governed by a rod descending through the pillar of the balance and resting on a simple eccentric, by the turning of which it is gradually raised or lowered. In the best balances too, a second eccentric, by means of two bent levers, raises supports beneath the pans of the balance, and either holds these safely while weights are being placed in them, or checks their oscillations preparatory to the release of the beam. The two eccentrics are so adjusted that on turning the handle, the pan supports are first rapidly dropped; the beam is then very gently lowered on to the centre plane; and lastly the pan-suspensions are in the most delicate manner left free upon the extreme edges, the beam being perfectly horizontal and undisturbed, so as not to show the slightest preponderance one way or another. Much of the excellence of a balance, as it is employed in chemistry, depends upon these several movements being smoothly performed, and the parts being released without the least stickiness; otherwise the beam is thrown into oscillation, and the true approach to equilibrium cannot be readily observed.

Most of the weight of the beam and frame is usually borne by a spiral spring in the interior of the column. An index moving over an ivory scale one inch long, divided into twenty parts, indicates the movement of the beam. The index should, of course, point exactly to the centre division, both before the beam is raised and when it is free and unloaded. The balance is enclosed in a glass case, with convenient windows, not shown in the figure; but when a very bulky object has to be weighed, the finger-screws at the base of the column (*fig.* 78) are to be loosened: the column and beam may then be turned through about 60°, so that the scales extend without the case. Two spirit-levels, or a circular level, and levelling screws, are attached by which the whole instrument must be adjusted to horizontality. Above the centre of the beam is a small weight, which we may call the *gravity-bob*, and which, being screwed up or down, regulates the stability of the balance, while a small *vane* being turned to the right or the left adjusts the beam to equilibrium. In the figure too will be seen an arrangement of rods, by which a small rider weight may be placed upon any part of the beam, the balance case remaining closed.

The balance above described is by Oertling, of Bishopsgate Street, London, who likewise constructs the chemical balance in seven different varieties more or less elaborate.

Fig. 80.

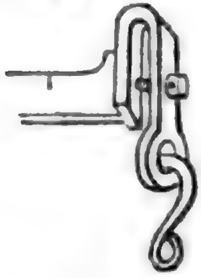


Fig. 81.

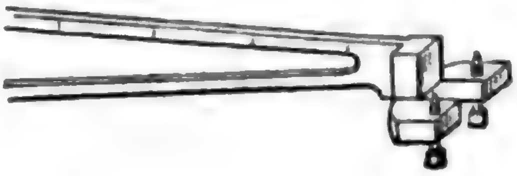
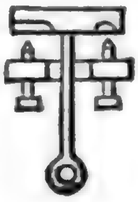


Fig. 82.



The largest of these, with a 16-inch beam, able to bear two pounds in each pan, and yet turn with $\frac{1}{100}$ grain is a remarkably fine instrument. The German balances made by Oertling of Berlin, Staudinger of Giessen, Steinheil of Munich, and others, are extremely delicate and well made instruments. Deleuil of Paris enjoys also a just celebrity for his chemical balances. M. Stas, in his late researches upon the atomic weights, employed a balance by Gambey, which turned to half a milligramme when laden with a kilogramme; also one by Sacré of Brussels, carrying two or three kilogrammes and turning with 0·3 milligramme. *Fig.* 83 shows the terminal suspension of a delicate balance by Fortin of Paris, capable of indicating one part in a million, while *fig.* 84 is from a German balance.

Fig. 83.

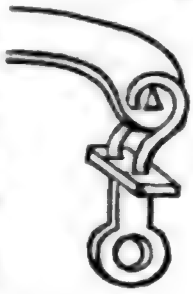
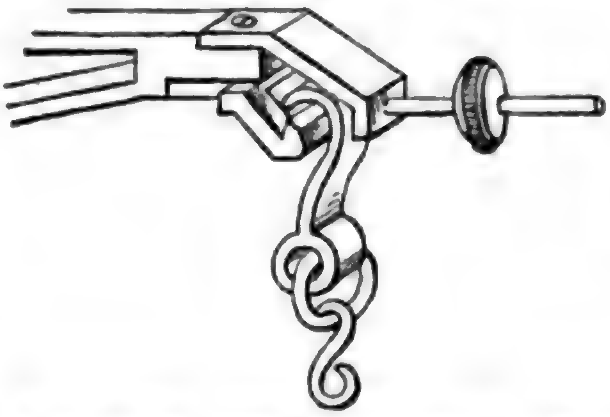


Fig. 84.



The Assay Balance is specially adapted for weighing small objects with great accuracy and rapidly. The French assay balances consist of a very light steel beam mounted in the manner of a pair of scales with hook pan suspensions, yet their performance is good.

Oertling constructs the assay balance in five forms, of which the most commonly employed has an 8-inch plain brass beam with a centre steel knife-edge and hook pan suspensions, adjustable by a small screw, as shown in *fig.* 80. It is not adapted to bear more than two grammes in each pan, and will perhaps indicate the $\frac{1}{20}$ part of a milligramme.

Another kind has an 8-inch perforated beam, with three agate edges and planes, and in fact all the elaborate movements and adjustments of the chemical balance above described, on a small scale. It will bear 10 or 15 grammes in each pan, and yet indicate surely and *rapidly* about $\frac{1}{20}$ of a milligramme.

Lastly, we may mention the 10-inch assay balance, with a very light perforated beam. A figure and a short description of this balance will be found under the article Gold Assay, but the terminal suspensions are shown here in *figs.* 81 and 82, and are formed of two small screws, bearing sharp points of ruby, one working into a little hollow, the other into a little channel in a steel cross-piece, from which the pan is suspended.

In contrast to the last balance it may be mentioned that Oertling constructs balances on the principles of the chemical balance with a beam 4 feet long, able to bear 2000 ounces in each pan, and yet turn with half a grain, or the one-millionth part of the load. They are chiefly employed in the several English and American mints for weighing bullion, but might be useful in some scientific investigations. See Jury Reports on the Great Exhibition of 1851 (p. 258).

It is of little use to describe forms of the balance which are now antiquated. Those by Robinson, by Ramsden, and his successor, Berge, and by Barrow, had beams composed of two hollow brass cones joined at the base with many elaborate adjustments. A balance made by Ramsden for the Royal Society is said to have indicated one part in seven millions. In the Göttingen Transactions, is described a balance constructed by Gauss and Weber, the beam and scales of which were poised on watch springs, a method contrived by Gauss. Beams suspended by ribbons, threads, or turning on little spheres of steel have been tried by Steinheil; but in no instrument have attempts to invent new forms been more futile.

The Adjustment of the Beam to the due degree of sensibility and accuracy has to be entirely performed by repeated trial-weighings, and requires the greatest skill.

Firstly, if the three edges of suspension are not already in one plane, but admit of adjustment, as is sometimes the case, proceed as follows:—Without weights in the pans poise the beam, and then raise or lower the *bob* until the vibrations are rendered very slow; now put weights into the pans equal to about half the greatest load the balance is to carry, so that the beam may be poised again; if it now vibrates slowly as before, it proves the adjustment to be perfect; but in case it either oversets or vibrates too quickly, restore it to slow motion by the adjusting weight or *gravity-bob*, as we may call it, noting the number of turns of the screw and parts of a turn which were required to produce slow motion; now turn the screw the contrary way, through double the noted quantity, and then produce the required slow motion by the proper adjustment at the end of the beam. Repeat the operation till the adjustment is perfect.

Secondly, to adjust the edges of suspension to equal distances; poise the beam with weights as in the last case, and then change the pans and suspensions from one side to the other. If equilibrium still holds, the adjustment is perfect; if not, take as much hair or wire as when put into the apparently lighter scale, will restore the balance; take away half of it, and poise the beam by the proper adjustment at the left end, which completes the process. Instead of placing any weights in the pans, all the poising may be conveniently done by a rider-weight on the beam, and in the last operation it is to be removed half way towards the centre of the beam. The adjustment of the edges to perfect parallelism is of course indispensable; we only presume that it is done by placing narrow planes or hooks on different parts of the edges and moving these until the apparent weight is the same on whatever part the weight bears.

A good balance in perfect adjustment should bear most of the following tests: Without weights, of course, it should remain with the index at zero, or make equal slow excursions on either side. The pans being removed, the beam alone should be in equilibrium, and oscillate probably much more quickly. If there be nothing in the construction of the balance to hinder it, the beam should be turned round from left to right and should act as before; this test is a severe one, generally disclosing as it does some defect in the work of the middle knife-edge and the planes on which it rests. If the pans and suspensions have been separately adjusted to equality, which is advantageous, although not quite necessary, equilibrium should hold when the pans and suspensions are variously changed in both positions of the beam. Lastly, the pans being fully and equally loaded, the weights should be changed from pan to pan, and equilibrium yet hold, proving the lengths of the arms to be fully equal.

A good balance, too, may be known by its giving the weight of an object, the same or nearly so, when weighed several times successively. There are few balances that will do this with certainty to the last minute fractions which they are capable of indicating.

Weights.—The results required by the chemist in analyses being merely comparative or proportional, the choice of a unit weight is a matter of indifference, provided that it be not varied during the progress of an experiment. But it is most convenient to adopt weights connected with some national standard, so that absolute weighings may if necessary be recorded. Grain weights are still sometimes used by English chemists, but most men of science of all nations appear by a kind of tacit agreement to have adopted the French standard weight, the gramme, with its uniform series of decimal multiples and submultiples; and we therefore strongly recommend its exclusive employment by every scientific chemist.

A complete set of weights extends from the smallest that the balance will indicate, up to the greatest that it will bear, and the series usually supplied with a balance is as follows:—

·001 gramme	·01 gramme	·1 gramme	1·0 gramme	10·0 grammes
·001 ,,	·01 ,,	·1 ,,	1·0 ,,	10·0 ,,
·001 ,,	·02 ,,	·2 ,,	1·0 ,,	20·0 ,,
·002 ,,	·05 ,,	·5 ,,	2·0 ,,	50·0 ,,
·005 ,,			5·0 ,,	

the whole making up just 101 grammes. These are arranged most conveniently in two little wooden stands, which may either be introduced into the balance case or enclosed together with the forceps in a separate box. A glass cover also lies over the small weights. The weights from 1 gramme upwards are best made of brass *gilt;* below 1 gramme, of platinum in the form of flat squares, with a corner bent up for holding in the forceps, the weight being stamped on each piece. The milligramme weights are sometimes made of palladium or aluminium; but the latter metal is rather too soft for the purpose, and is apt to wear away.

An admirable improvement in the modern balance consists in its partial employment on the principle of the steel-yard, as far as regards the estimation of the last minute fractions. A small *rider*, or hanging weight of thin gold (or brass) wire, is placed upon the upper edge of the beam either by the forceps, or more conveniently without opening the case, by a brass sliding rod and a little arm (see *fig.* 78), on either side of the beam. Now the weight which this rider exerts towards turning the beam is such a fraction of its whole weight in the pan, as its distance from the centre of the beam is of the distance of the pan-suspension from the centre. The rider commonly weighs ·01 gramme, and each arm of the beam is graduated into twenty parts; but the fifth part of these divisions may easily be guessed, so that the fractional weight may really be read off to the $\frac{1}{100}$ part of the rider weight, or ·0001 gramme. This simple contrivance, compared with the use of minute weights in the pans, presents the following advantages.

1. Saving of much time and trouble. 2. Greater accuracy, small weights being liable to collect dirt, or to be rubbed or injured. 3. Minute estimation of weights to any required degree. 4. Diminished chance of error in reading off the weight. With numerous small weights errors are *certain* frequently to occur.

The series of grain weights 1, 2, 3, 4, 10, 20, 30, 40, &c. is not uncommonly employed, and is quite as convenient as the series 1, 1, 2, 5, 10, &c. As a curious fact, it may be mentioned, that the series of powers of 3, viz. 1, 3, 9, 27, 81, affords the greatest number of combinations to a given number of weights. Thus twelve such weights give by *addition or subtraction*, any integral number from 1 to 265,720, while 21 weights of the series, 1, 1, 2, 5, do not reach 200,000.

Weights when used in a laboratory must almost always become too light by wear, or more commonly too heavy by corrosion of the brass. Were the error always proportional to the size of the weight, all error would be eliminated in any comparative result. But this is not usually the case, since the mass increases as the cube, while the surface increases as the square of the diameter. Hence the small weights will be more erroneous in proportion than the large. Weights should never be rubbed, and if dusty, should be wiped with a silk handkerchief or a camel's-hair brush. Small *platinum* weights may be cleaned if necessary, by momentary exposure to the flame of a spirit-lamp. One set of weights should, if possible, be carefully preserved beyond the influence of fumes, and should not be touched but by ivory-pointed forceps. The weights commonly used should occasionally be tested against these, to see whether their errors be disproportionate; or weights may less satisfactorily be tested against each other. An experienced weigher will never trust even the best balance maker as to the accuracy of his weights, but will always test them against each other in various ways, on first receiving them. Many conclusions, observes Faraday, tending to subvert most important chemical truths, might be quoted as having arisen solely from errors in weights and balances.

In assaying (see Gold Assay), a special unit and set of weights is adopted to suit the weighings required; the same might be advantageously done in any large set of analyses or experiments.

Much time will on the whole be saved in weighing, if the weights be taken methodically in their proper order, 10, 5, 2, 1, 1, except, of course, the slow motion of the balance indicate that only a small weight more should be added. For if an unknown weight exceed 10 but fall short of 20, it is an even chance that it be above or below 15, so that if the weights 2, 1, 1, be used after the 10, it is *as likely as not* that the weigher will lose his trouble, and have to resort to the weight 5. In this respect the series of weights (avoirdupois) 16, 8, 4, 2, 1, $\frac{1}{2}$, $\frac{1}{4}$, &c. is obviously the most advantageous.

When equilibrium is nearly attained, the expert weigher will notice the rapidity with which the index of the beam traverses the arc, or the extent of the oscillation if it be less than the whole arc, and comparing this with the load in the pans, and with his previous experience of the same balance, will closely estimate the alteration of weight required, and thus save half the time and trouble which the adjustment would otherwise have occupied. It will afterwards be shown that the oscillations of a good balance may give sure determinations of the most minute fractional weights.

We cannot too strongly impress upon the reader the danger of mistakes in reading off the weights in the pan of a balance. The danger is greater with small than with large weights, and this alone would be sufficient reason for the use of a rider weight. In any case, the weights in the pan should be read, then taken out and arranged in order, and again read; lastly restored to the pan, and fresh trial made. Or the reading of the weights may be compared with the vacancies in the box of weights. When the vibrations of the balance have to be read, the divisions of the scale should be numbered from left to right continuously. For if the zero be in the centre, the signs + and − must be used, and mistakes are sure to occur. Under the article Gold Assay will be found an instance in which vibrations are used with great convenience in estimating the last fractions of weights.

The casual sources of mistake are too many to mention. Not unfrequently a rider may remain unnoticed on some part of the beam, and vitiate several weighings. When a bulky or flexible object is being weighed, some part is very likely to come in contact with the balance case. We have even known a scrupulously exact gold-assayer led into serious mistakes by a small fly, which settled on his balance, unobserved at the time.

An object heated many degrees above the temperature of the air, cannot be accurately weighed; for it is surrounded by ascending currents of air, which cause its apparent weight to vary every moment, and it is very likely to heat and expand unequally the arms of the beam above. Special modes of weighing hygroscopic substances, liquids, powders, gases, &c., must be adopted according to the nature of the case; the chemist must generally depend for these on his own ingenuity, but will find many valuable directions in Faraday's Chemical Manipulation, section II., also in Greville Williams's Chemical Manipulation.

If we have to compare the weights of any two objects, A and B, which are held or accompanied by other objects, X and Y, the weights of the latter may be perfectly eliminated if each of A and B be weighed as often in X as in Y, and the mean result taken.

We will make the following suggestions for the care of a balance.

1. It should never be moved, if possible, from its appointed place; for this would not only disturb its adjustment to horizontality, but the swinging and shaking of the pans and beam would be likely to injure or slightly alter the condition of the balance. The operator too will never weigh so well as in a place, and with a light to which he is accustomed.

2. The balance should not be cleaned or altered often or hastily. A good cleaning, once every three months, for instance, is enough, if the balance case be kept well closed. An hour or sometimes two or three, may well be spent in the operation of cleaning. All the loose parts should be carefully taken out and dusted; the movements cleaned and fresh oiled; the suspensions polished with a piece of soft leather. Then all the parts are to be put together again, and brought to elaborate adjustment, which with careful usage will be maintained for some months.

3. The chemist should be perfectly acquainted with the capacity, the general character, and also the particular condition, at any moment, of each of his balances.

4. Before every weighing, or set of weighings, he should try whether the unloaded balance is in perfect equilibrium; if not, he may brush the pans or beam with a camel's hair brush, to remove dust, or if he dust the preponderating side only, it will often restore equilibrium. He should not touch the little regulating vane, or alter any part of the balance, without being satisfied that some special cause for it has arisen. The one great essential of accuracy is perfect uniformity in everything but the thing to be measured, and no one can have faith in a measuring instrument which is always changing.

5. It is almost needless to say that a balance, especially one with steel knife-edges, must be kept beyond reach of all acid fumes or damp. A small vessel of quick lime or chloride of calcium should be in the balance case, and this should be kept constantly closed.

All weighing out of reagents, where a grain more or less is not material, should be made with common apothecaries' scales on the laboratory table.

A balance should be placed in a good light, falling if possible over the right shoulder of the operator. But it may also with advantage be placed before a window, provided that a purple silk shade be used. The purple light thus thrown behind the balance is subdued, agreeable, and complementary to the yellow of the brass. As a general rule, the object to be weighed should always be placed in the left hand pan, which we may hence call the *object-pan*. The other, or *weight-pan*, will thus be conveniently opposite the right hand. In assaying, this arrangement is reversed.

The number of balances required in a chemical laboratory may vary from one to twenty, or more, according to the size and purposes of the laboratory. For the common operations of quantitative analysis, the chemical balance first described is alone necessary. A larger balance will, however, be almost indispensable in water-analyses, and in many physico-chemical investigations, and will always be advantageous by allowing the use of large evaporating dishes and vessels, or the weighing of a series of drying tubes, or other apparatus as a whole. But a laboratory is not complete without an assay balance, which will perform all light weighings with an accuracy and expedition impossible in a large balance.

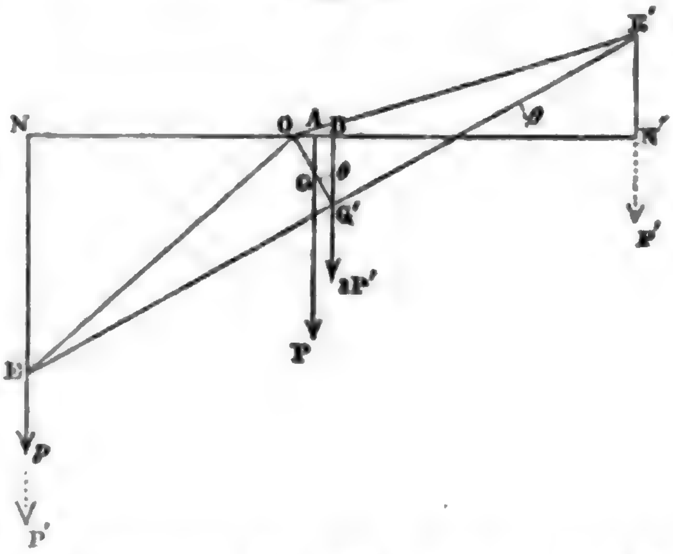
When the employment for balances is very extensive, it will be best accommodated, not so much by increasing the number of balances as by classifying them, assigning to each its proper work, and strictly adhering to rules once laid down. Where there are two balances of the same kind, it is obviously best to retain one for the more refined purposes, and make the other perform all common work, and two balances thus used may serve better than half a dozen indiscriminately worked and spoiled.

Mechanical Theory of the Balance.

Properly to understand the action of a balance, it must be considered both statically and dynamically, that is to say, both when the beam is at rest and while it is in motion; for the oscillations of a good balance are almost as valuable an indication as its position at rest.

First, however, to show the conditions of equilibrium, let O (*fig.* 85) be the central axis of suspension of a balance, and EE', the extreme axes of suspension not necessarily in the same straight line with O. Suppose equal weights, each = P', to act at E and E', including of course the whole weight of the burthen, pans, and other objects suspended at the extreme axes. Then the whole weight $2P'$ may be conceived as acting at G', the middle point of the line EE'. Assuming the axis O to be properly placed at equal distances from E and E', the line OG' will be perpendicular to EE', and the weight of the beam, say P, will act at its centre of gravity, which is, or should be, some point G, on this line or its prolongation.

***Fig.* 85.**



Lastly, let some small additional weight p act at E. The beam can not now remain horizontal, but may again rest in equilibrium in some position inclined at an angle, say θ, to the horizontal line NN'. Drawing E N, E' N', G A, G' B, perpendicular to NN', we must have, according to the principle of the lever, the sum of the moments of the forces on one side equal to that on the other, or

$$2P'.\mathrm{OB} + P.\mathrm{OA} = p.\mathrm{ON} = p(\mathrm{BN}-\mathrm{BO})$$

Or, substituting in terms of θ, we have

$$2P'.\mathrm{OG}'.\sin\theta + P.\mathrm{OG}\sin\theta \quad = p.\mathrm{G'E}.\cos\theta - p.\mathrm{OG}'.\sin\theta$$

$$\tan\theta = \frac{\sin\theta}{\cos\theta} = \frac{p.\mathrm{G'E}}{(2P'+p)\mathrm{OG}'+P.\mathrm{OG}}$$

Now for small values, $\tan\theta$ varies very nearly as the angle of deviation θ, which angle may be regarded as the true measure of the sensibility of the balance, and p being quite inconsiderable compared with $2P'$ and P, we may say that *the sensibility is increased by increasing the length of the beam, diminishing the weights of the beam and load, or diminishing the distances of G and G' from the axis O*, and also that *the sensibility varies very nearly in the direct or inverse ratio of these changes.*

Again, the force tending to restore the beam to the horizontal position when disturbed is $\sin\theta\,(2P'.\mathrm{OG}' + P.\mathrm{OG})$. This is the measure of the *stability* of a balance, a certain degree of which is required to render a balance useful. Now with given weights P and P', and for any given deviation θ, the force of stability will entirely depend upon the positions of G and G', and the following are the cases which arise.

1. The extreme points of suspension EE' may be so placed that G' falls above O. The stability is $\sin\theta\,(P.\mathrm{OG}-2P'.\mathrm{OG}')$, which for a certain value of P' will be *nothing*, so that the whole system will be suspended at the centre of gravity, and the beam being disturbed will have no tendency to return, but will rest in *neutral equilibrium*, indifferently in any position.

For a greater value of P', the force will be *negative*, and the equilibrium unstable, that is to say, the beam when loaded beyond a certain degree will *overset*, and permanently sink down on one side without a tendency to return, even when the weights on the two sides are not unequal. A balance of such construction then, could only be used for weights of a certain smallness, and its *sensibility* would increase and its stability decrease with its load.

2. If G fall above O and G' below, the stability is $\sin\theta\,(2P'.\mathrm{OG}-P'.\mathrm{OG})$, which will be *nothing* for a certain value of P', and negative for smaller values. The balance

then would be *stable* only when P', the load in the pans, is not less than a certain magnitude.

3. If G coincide with O (OG = 0) and G′ fall above O, the balance is always unstable and useless.

4. If G coincide with O and G′ fall below O, the stability is $2P' . OG' . \sin\theta$, which depends entirely upon the weight placed in the pans.

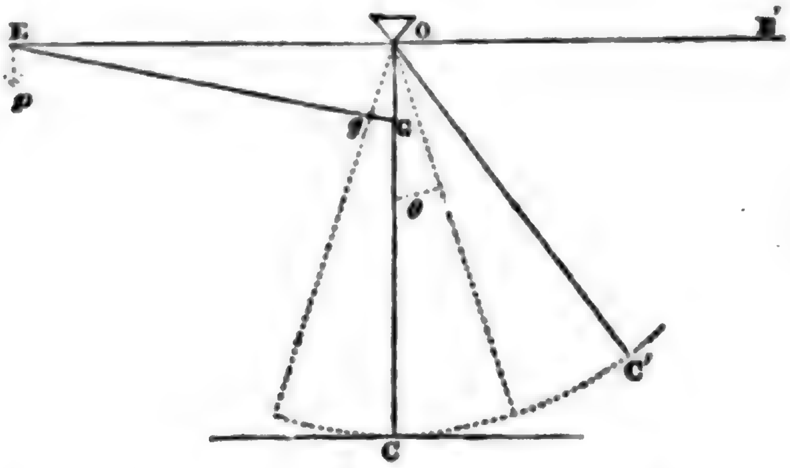
5. Now let G′ coincide with O, (OG′ = 0) the three points EOE′ being in a straight line, but let G fall below O. The stability is $\sin\theta . P . OG$, which for a given value of OG, is constant. Also $\tan\theta = \frac{p . OE}{P . OG}$ which depends only on p. In a balance of such construction, all weights may be weighed indifferently and with equal accuracy, and any required degree of sensibility may be obtained by duly regulating the length of OG.

6. Let G and G′ coincide; then $\sin\theta . OG(2P' + P)$ is the measure of stability, and is proportional to the weight to be moved. Also $\tan\theta = \frac{p . GE}{(2P' + P + p)OG}$ varies inversely as the total weight moved.

In any case of stable equilibrium, it will be easy to determine the position of the centre of gravity (say g) of the *whole system* from the formula $Og = \frac{p . OE}{\tan\theta(2P' + P + p)}$ by observing the deviation for several values of p, and for a given load P' in the pans. A different value will be found for Og for each different value of P′, unless the balance be constructed in the sixth mode described above. In a sensitive balance Og, will probably not exceed $\frac{1}{10000}$ part of an inch.

We may now consider the balance in the character of a compound pendulum, selecting for this purpose the fifth mode of construction above described. Thus if G, the centre of gravity of the beam (*fig.* 86), be vertically under O, and the weights in the pans be equal, the system will be at rest. But now suppose a small additional weight p added at E: the centre of gravity is no longer at G but say at g, nearer to E by a distance (Gg), such that

Fig. 86.



$$\frac{p}{P} = \frac{Gg}{gE} = \frac{Gg}{GE - Gg} \text{ or } Gg = \frac{p . GE}{P + p}$$

Since g is not vertically under O, the beam cannot remain at rest, but will vibrate about the perpendicular line OG, and the point C of the index fixed to the beam will describe the arc CC′, subtending the angle 2θ.

The velocity of the beam is greatest, of course, when g is vertically under O, and being proportional, as proved in the theory of dynamics, to the angle θ, is also nearly proportional to p. Hence when the deviation is small, *the greatest velocity which the beam attains may be observed as an indication of p.*

As in any other pendulum, the length of time occupied in a vibration is almost the same whether the vibration be great or small, as may easily be observed to be the case.

Fully to understand the motions of a beam, it would be necessary to determine its *moment of inertia round the axis*, which is the sum of the moments of each particle, the moment of inertia being the mass of a particle multiplied by the square of its distance from the axis. The velocity of the beam depends on the proportion of the force of stability or the force of disturbance, and the moment of inertia, which it has to overcome. Hence the force of stability alone gives a very imperfect idea of the motion of the beam, which will be slower the greater the weight in the pans, especially if the force of stability itself be not increased, as in the sixth case, by increasing the weight in the pans.

The mechanical problem of the balance is not so simple as may at first sight appear, and has not, so far as we are aware, been properly considered dynamically. The problem of the compound pendulum, will be found best treated by Poisson (Traité de Méchanique, t. ii. c. i. § 3). Euler, in the Petersburg Commentaries (x. 3), appears to have shown the statical conditions of a balance.

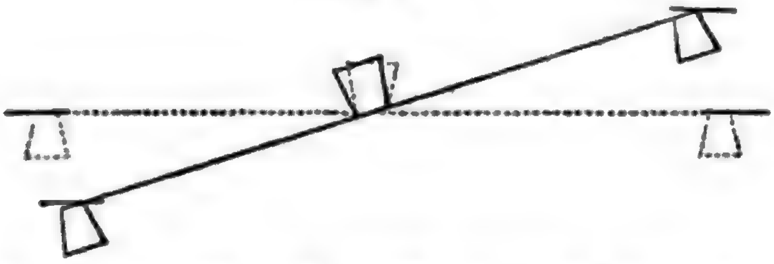
It will be apparent that, the length of the beam remaining constant, the properties of statical sensibility and stability are reciprocal to each other. By increasing the length of the beam, indeed, the balance is said to be rendered both more sensible and stable. But in reality the weight of the beam must be increased in a far greater proportion than its length, so that its motions will become much slower, to say nothing of the less convenience of a large instrument.

The construction in which the three axes are in one straight line, is undoubtedly the most perfect, and is especially suitable if the vibrations are to be used, as afterwards described, for the determination of fractional weights. But a balance in which the centre axis is slightly above the line of the extreme axes, will not become so much slower in its movements when heavily laden, and will yet indicate at least as small a fraction of its load when this is great, as when small. Hence such a balance will, we think, be suitable for most purposes. It is necessary however to bear in mind, that when the three points of suspension are not in one straight line, equilibrium may subsist when the beam is not horizontal, and the *weights in the pans are unequal*. For when the angle EON is greater than the angle E'ON', ON and ON' are unequal, and we may have equilibrium for $P' . \mathrm{ON} = P'' . \mathrm{ON}'$, where P' and P'' are unequal weights in the pans.

The truth is, that a balance must be so adjusted in its length, strength, weight, and relative position of the centres of suspension and gravity, as to combine the exact degrees of sensibility, stability, or quickness, and capacity for bearing weights, which its special employment requires. In this adjustment, the chief skill of the balance maker consists. Diminution of weight of the beam is an unqualified advantage, as long as the strength is sufficient. Thus the employment of aluminium in the construction of balances, will be of great advantage when accomplished; but an aluminium beam, which we have seen, was stated not to be trustworthy in point of strength and inflexibility.

The impediment to the free motion of a beam, is usually stated vaguely to be the *friction* at the knife edges. But although friction or adhesion may be of some importance, the variation in the length of the arms has really a much greater effect. Thus, suppose, as is generally the case, that the knife-edges, instead of being perfectly sharp or round, terminate in very narrow planes (*fig.* 87), of the width x. If the distances between the middle points of the knife edges be a, the real lengths of the two arms of the lever when the beam is not horizontal, will be $a-x$, and $a+x$, consequently weights which have the ratio of $a+x$, and $a-x$, may be apparently in equilibrium. In order then that a balance with a 20-inch beam may indicate the millionth part of its load, we must at the most have $\frac{1,000,000}{1,000,001} = \frac{a-x}{a+x}$ or $x = \frac{10}{2,000,001}$ inch; within the same length too, the two arms of the beam must be adjusted to equality if the balance is to be accurate within one millionth part of its load. Now this length, being inappreciable in a common microscope, will give some idea of the skill required in a balance-maker. We are thus prepared too for the statement of Prof. Miller (see reference below), that he not only detected a difference in the expansion of the arms of his balance by a change of temperature, owing to some difference in the quality of the metal, but that temperature also affected the sensibility of the instrument, which resembled an *over-compensated pendulum*, from the difference of expansion of the steel knife edge and the brass in which it was fixed.

Fig. 87.



The resistance of the air has but an inconsiderable effect upon a balance.

Elimination of Errors.—Since every balance however good, requires some *definite* weight to cause it to turn, a difference of this amount may exist between any two weights which are apparently in equilibrium. Thus if a balance when loaded refuse to turn with anything less than $\frac{1}{10}$ of a grain, it is an even *chance*, that two weights which do not cause the balance to move, differ by $\frac{1}{20}$ of a grain or more. In the common use of a balance, the turning-weight (*scrupulum* in Latin), will give the limit of accuracy of the weighings. Let this turning-weight be Δx; then the balance will turn when the weights $x + \Delta x$ and x are in the pans. It will also probably turn in the opposite direction when $x - \Delta x$ is substituted for $x + \Delta x$, because the balance, unless a very bad one, will turn as easily one way as the other. Thus the mean of $x + \Delta x$ and $x - \Delta x$, will be the true weight required, nearly freed from the error of insensibility. This operation may be resorted to when a balance has become insensible by age but is otherwise good, and may be very easily performed by the use of a rider weight. But the delicacy of balances is generally ahead of what is required of them. Any good balance should weigh with certainty to the $\frac{1}{100000}$ part of its load, but there are as yet few chemical operations which can pretend to an accuracy of $\frac{1}{10000}$ part.

The only other kind of error to which the determinations of a balance are essentially liable, is that caused by the inequality of the arms: for the extreme edges can never be adjusted at perfectly equal distances from the centre edge. This error is avoided entirely and without trouble, in the ordinary operations of the chemist, by taking care, during each analysis or series of experiments, to use, say the left pan invariably for the objects to be weighed, and the right pan for the weights. The apparent weights of all the objects are thus increased or diminished in precisely the same ratio, and the comparative results are therefore unaffected by the real falsity of the balance.

Thus if a be the length of the arm bearing the weight-pan, and b the length of that bearing the object-pan, then objects of the true weights, x, y, z, &c. will appear to weigh $\frac{b}{a}x$, $\frac{b}{a}y$, $\frac{b}{a}z$, but the ratios $\frac{b}{a}x : \frac{b}{a}y : \frac{b}{a}z$ are the same as $x : y : z$, the ratios of the true weights. That this elimination of error may be perfect, it is obviously necessary that no weights be placed in the object-pan, as is sometimes done, for the purpose of making up a given weight in the easiest manner by subtraction.

There are, however, two well known methods for obtaining the true absolute weight of an object, even by a false balance. The first, introduced by Gauss, proceeds by simply weighing the object alternately in one pan and the other. If the apparent weights are the same, they are each the true weight, or the balance is appreciably correct. If not, the geometric mean is the correct weight, and is found by multiplying the true apparent weights together, and taking their square root. For if the true weight be x, and a, b be the lengths of the balance arms as before, $\frac{a}{b}x$, and $\frac{b}{a}x$ will be the apparent weights in the respective pans, and $x = \sqrt{\frac{a}{b}x \cdot \frac{b}{a}x}$. If the apparent weights be very nearly equal, their common arithmetic mean $\frac{1}{2}\left(\frac{a}{b}x + \frac{b}{a}x\right)$ is quite close enough to the truth. Thus the arithmetic mean of 1·000 and 1·001 is 1·0005, and the geometric mean 1·0004998 . . . .

The second method for ascertaining absolute weights free from all error, is that known as the *method of substitution*, ascribed by French writers to Borda, but probably due to the Père Amiot. If there be one weight C in the weight-pan, and other weights X, Y, Z, &c. be in succession placed in the object-pan, and the balance is yet always in equilibrium, it is evident that $X = Y = Z = \frac{b}{a}C$. Thus we prove the perfect equality of X, Y, Z, although each of these may differ in an unknown degree from C, owing to the inequality of b and a, the lengths of the balance-arms.

To compare the weights of any two objects by this method, counterpoise the greater with the weight C, made up of shot, tin-foil, wire, or any convenient substance. Then substitute the second object for the first, and observe how many small weights must be added to the pan to restore equilibrium with C. The only errors which can affect such a result will be that of insensibility, and any error which may arise from a minute change of the edges of suspension during the substitution; but these errors may be eliminated by taking the mean result of many such operations, a new counterpoise being adjusted each time.

But when important weighings have to be made with the most rigorous accuracy, as in the comparison of standard weights, the method of vibrations must be resorted to. This being a process of pure observation, as distinguished from one of adjustment, admits of unlimited approach to absolute exactness, just as the difference of two standard yards may be ascertained to the $\frac{1}{1000000}$ part of an inch, although it would be impossible to make two yards agree within ten times that quantity.

The paper by Prof. W. H. Miller, on the Construction of the New Imperial Standard Pound (Phil. Trans. cxlvi. (1856) p. 753), should be studied by all engaged in exact determinations of weights, but a more explicit account of the method of vibrations will be found in Kupffer's work, "Travaux de la Commission pour fixer les Poids et Mesures de Russie," St. Petersburg, 1841. Prof. Miller's mode of observing the oscillations appears to be the most eligible. His balance had a very light ivory scale, about half an inch long, divided into spaces of about $\frac{1}{100}$ inch, *attached* to the right end of the beam. This scale, as it moved, was viewed through a fixed compound microscope, having a single horizontal wire in the focus of the eye-piece. A still more delicate mode of observation, is by a small mirror fixed to the beam, in which the reflection of a divided scale is viewed through a fixed telescope, as in the instruments of a magnetical observatory.

The weights to be compared being very nearly in equilibrium, the balance when released oscillates slowly through a very small arc, and the extreme points of each excursion are to be observed. Supposing the readings thus observed to be R^1, R^2, R^3, R^4. Then $\frac{R^1 + 2R^2 + 2R^3 + R^4}{6}$ is the position of equilibrium of the beam: for, by the nature of the pendulum already considered, the excursions will be as far on one side as on the other. In this expression, R^2 and R^3 are doubled, because they are the end of one half vibration and the beginning of another. Prof. Miller usually rejected the first reading because it is apt to exhibit slight irregularities, and his result was derived from $\frac{R^2 + 2R^3 + R^4}{4}$. This observation completed, a small known weight is added to the lighter of the weights compared, and the new position of equilibrium which the beam tends to take up, is observed by a new set of readings. Now the deviation from the horizontal position in a good balance being very nearly proportional to the weight causing it, we obviously learn from the angular difference of the two positions of the beam, the deviation corresponding to a given small weight. Hence we learn by the simplest calculation the difference of weight corresponding to the deviation in the first observation.

The method of weighing by reversal was found more convenient by Prof. Miller, than that by substitution, and was thus practised.

The nearly equal weights P and Q to be compared, were weighed directly against each other, but repeatedly reversed, and the balance was so adjusted by a small constant weight placed in one of the pans or on the beam, that on interchanging P and Q, the position of equilibrium was still near the middle of the scale. Then if (P, Q) be the reading of the scale in the position of equilibrium when P is in the left hand pan, and Q in the right hand pan, and (Q, P) the reading when Q is in the left hand pan, and P in the right hand pan; then $2Q = 2P + m((P, Q) - (Q, P))$, where m is the weight equivalent to one degree of deviation on the scale.

In the determination of the equivalents of the elements, and in many physico-chemical determinations, it is to be hoped that chemists will soon have to tax to the utmost these refined methods of weighing.

On the balance generally, the reader may further consult Biot, Traité de Physique, i. 9; Pouillet, El. de Phys. i. 66; Ann. de Chim. xxxvi. 3; Jury Reports on the Exhibition of 1851, pp. 257—262; Phil. Trans. cxvi. pt. 2, p. 36. For a description of Napier's "Automaton-balance" for weighing coin, see *Ure's Dictionary of Arts, Manufactures and Mines*, i. 245. W. S. J.

BALLUS, or BALAIS RUBY. A variety of spinelle, varying in colour from reddish-white to pale red.

BALLESTEROSITE. A variety of iron pyrites, found in Asturia and Gallicia, Specific gravity 4·75 to 4·90.

BALLOON. Receivers and flasks of spherical form are sometimes called balloons.

BALSAM. This term, originally confined to a single substance, viz. Balm of Gilead, Mecca Balsam, or Balsam of Judea, is now extended to a variety of products, more or less resembling that body, but exhibiting considerable diversity of composition and properties. They are viscid, aromatic liquids, which exude from growing plants, either spontaneously, or from incisions made for the purpose.

Balsams are mixtures of resins with volatile oils, the resins being produced from the oils by oxidation, so that a balsam may be regarded as an intermediate product between a volatile oil and a perfect resin. They may be divided into two groups, the one including those of purely oleo-resinous character, viz. *Copaiba balsam*, *Mecca bal-*

sam, and the *balsams* or *turpentines* of coniferous plants; the other group, including those which contain cinnamic acid, such as *Peru balsam*, *Tolu balsam*, *Liquidambar*, and *Storax*. Benzoin and Dragon's-blood are sometimes also classed among balsams; but they are more properly resins; the true balsams are liquids more or less viscid, and yield volatile oils by distillation with water. The balsams of the second group yield by dry distillation, cinnamate or benzoate of ethyl or methyl, and according to Scharling, these products, or perhaps others not previously existing in the balsams, may be formed from them by the action of aqueous alkaline leys.

Balsams of the First Group: Oleo-resins.

CANADA BALSAM or **CANADIAN TURPENTINE**, *Baume du Canada*, is the produce of *Abies balsamea* (Dec.), a coniferous tree growing in Canada, Virginia, and Carolina. It collects in vesicles under the bark, and is obtained by making incisions in the stem. It is either colourless or slightly yellowish, rather mobile, but tenacious and capable of being drawn into threads, turbid when fresh, but soon becomes perfectly transparent when left at rest. It turns the plane of polarisation of a luminous ray to the right, and has an index of refraction equal to 1·532. It dries up to a hard varnish when exposed in thin layers to the air for about forty-eight hours, and gradually thickens, even in closed vessels. Its power of hardening, its transparency, and its peculiar refractive power, which is nearly the same as that of crown glass, renders it very useful as a cement in the construction of optical instruments. In some countries it is used as a medicine; when taken internally, it imparts a nutmeg odour to the urine.

Canada balsam distilled with water, yields a volatile oil, of balsamic odour, agreeing in composition with oil of turpentine (Wirzen), and like that oil, turning the plane of polarisation to the left (Biot); it also leaves a resinous cake, brittle after cooling, and consisting of a mixture of several substances. The balsam is partially soluble in alcohol, a granular resin remaining undissolved.

Canada balsam contains, according to Bonastre (J. Pharm. viii. 572 [1822]), 18·6 per cent. volatile oil, 40·0 resins easily soluble in alcohol, 33·0 resin sparingly soluble in alcohol, together with 8·4 caoutchouc and bitter extractive matters soluble in water. The sparingly soluble resin is described as dry, friable, heavier than water, difficult to melt, and becoming electrical by friction. According to Caillot (J. Pharm. xvi. 436 [1830]), the balsam contains two neutral resins, one called *abietin* (see p. 1), being crystallisable and easily soluble in alcohol of 0·824, the other white, pulverulent, without crystalline form, very little soluble in alcohol of 0·824, or in rock oil, or potash-ley, and closely resembling the sparingly soluble resin obtained from other species of abies; also an acid resin, which forms a coherent paste when mixed with $\frac{1}{10}$ of its weight of magnesia, and imparts to Canada balsam the property of forming a white soap with potash. According to Wirzen (*De balsamis et præsertim de balsamo Canadense Dissertatio*, Helsingforsææ, 1849), Canada balsam contains 16 per cent. of volatile oil, 30 pts. of a resin α, soluble in boiling alcohol of 0·833, and containing $C^{40}H^{62}O^4$ (78·31 per cent. C and 10·08 H), 33 pts. of another resin β, insoluble in hot alcohol, but soluble in ether, and containing $C^{40}H^{60}O^5$; and, lastly, 20 pts. of a resin γ, insoluble in alcohol and ether. Wirzen's α resin is probably a mixture of abietin with an acid resin.

A balsam exactly resembling the preceding, excepting that it has a darker colour, is obtained from *Abies canadensis* (Link). Canada balsam is distinguished from all other varieties of turpentine by its peculiar odour, its perfect transparency and ductility, and the facility with which it hardens when exposed to the air. Strasburg turpentine, from *Abies pectinata*, which very much resembles it, is distinguished by its optical lævo-rotatory power; and Venice turpentine (from *Larix europæa*), by its easy and complete solubility in alcohol of ordinary strength, and its indifference towards calcined magnesia.

The other balsams, or turpentines, derived from coniferous plants, will be described in the article TURPENTINE.

COPAIBA or **COPAIVA BALSAM.** *Balsamum Copaivæ*, *Baume de Copahu.*—This balsam is produced by several species of *Copaifera* (order *Cæsalpineæ*), particularly by *Copaifera bijugal*, Willd., *C. multijuga*, Hayne, *C. Guianensis*, *C. Langsdorfii*, and *C. Jacquini*, Desf., which are indigenous in Brazil, Peru, Mexico, and the Antilles. It is obtained by making incisions or perforations in the trees during rainy weather, and flows so abundantly that a single incision often yields 12 pounds of the balsam.

Copaiba balsam consists of several resins dissolved in a volatile oil, the amount and nature of the resins varying considerably in balsam from different sources. There are three principal varieties, the Brazilian, the Antillian and the Columbian.

Brazilian copaiba is light yellow, generally transparent, of various degrees of consistence, from mobile to syrupy, and of specific gravity ranging from 0·920 to 0·985. It has a peculiar, aromatic, disagreeable odour, and a persistently bitter and irritating taste. By exposure to the air, it becomes darker in colour, of the consistence of turpentine, heavier than water, and ultimately solid and inodorous. When heated in contact with the air, it takes fire and burns with a bright, but very smoky flame. The balsam from the Antilles differs from the Brazilian by its more viscid consistence, darker colour, imperfect transparency, and turpentine-like odour. Columbian copaiba is distinguished by its turbidity, arising from suspended particles of resin, which are deposited as a crystalline crust when the balsam is left at rest.

The chemical examinations hitherto made of copaiba balsam relate chiefly to the Brazilian, of which two varieties are distinguished.

I. *Copaiba balsam chiefly containing acid resins.*—This variety, which was formerly the only one known, is distinguished by the following characters:—It is insoluble in *water*, but imparts to the water its taste and smell. It dissolves in all proportions in *absolute alcohol*, in *ether*, and in *oils*, both fixed and volatile; the alcoholic solution, however, is often rendered turbid by the separation of resinous flakes. Alcohol of 90 per cent. dissolves a large quantity of it; alcohol of 80 per cent. only $\frac{1}{10}$ to $\frac{1}{2}$ of its own weight. Mixed with an equal weight of fixed oil, it dissolves in 2 pts. of 90 per cent. alcohol, the fixed oil separating only on the addition of a considerable quantity of alcohol. It absorbs *chlorine gas*, becoming turbid at the same time, from formation of hydrochloric acid. With *strong sulphuric acid*, it assumes a red colour and viscid consistence, with evolution of sulphurous anhydride, and an odour of oil of amber. *Strong nitric* acid acts upon it with violence; dilute nitric acid more quietly, forming a hard yellow resin, which dissolves partially in the acid, and a yellow bitter substance insoluble in water and in alcohol. Distilled with 2 or 3 per cent. of its weight of strong *sulphuric acid* or with *hypochlorite of calcium*, it yields a volatile oil of fine blue colour (Löwe, Pharm. J. Trans. xiv. 65); the same oil is said to be produced by the action of acid chromate of potassium. Three pts. of the balsam mixed with 1 pt. of *potash-ley* containing $\frac{1}{8}$ pt. of hydrate of potassium, yield a clear liquid, which does not lose its transparency when mixed with alcohol or with a small quantity of water, but becomes milky on addition of a large quantity of water. A larger quantity of caustic potash-ley added to the clear liquid, throws to the surface a transparent copaiba-soap, which forms a turbid solution with a large quantity of water, or with absolute alcohol, but dissolves completely in ether or in hydrated alcohol. When an alcoholic solution of the balsam is mixed with dilute potash or soda-ley, a volatile oil rises to the surface, while the resulting compound of resin and alkali remains dissolved in the hydrated alcohol. This process may be used for the preparation of the volatile oil. Five pts. of the balsam form with 2 pts. of aqueous *ammonia* of specific gravity 0·921, a clear mixture, from which a larger quantity of ammonia separates a soapy compound. A mixture of 9 pts. of the balsam and 2 pts. aqueous ammonia well shaken up and left at rest at + 10° C., gradually yields a crystalline deposit, consisting of the resinous acid of the balsam. The balsam likewise combines readily with *magnesia*. It dissolves completely $\frac{1}{30}$ of its weight of calcined magnesia, and when mixed with $\frac{1}{16}$ of its weight of that substance, thickens to a stiff paste in the course of a few days; with $\frac{1}{8}$ in a few hours. Similarly with *quick lime*. Carbonate of magnesium likewise forms with 4 pts. of the pure balsam at mean temperatures (15° C. or 60° F.), a clear viscid solution.

The balsam distilled with *water* yields a volatile mobile oil, C^5H^8, possessing in a high degree the peculiar odour of the balsam, and forming a crystalline compound with hydrochloric acid (see COPAIBA OIL), while in the retort there remains a mass of brittle resin, which is resolved by treatment with rock-oil, into a crystallisable portion soluble in that liquid (the α resin of Berzelius), and an insoluble unctuous substance (β resin of Berzelius). The crystallisable resin has the formula $C^{20}H^{30}O^2$, and from its property of reddening litmus and uniting readily with acids, is called *copaivic acid*. The crystalline deposit which separates from the turbid balsam, is, according to Fehling's investigation, a resinous acid containing $C^{20}H^{28}O^3$. It is to these two resins that the peculiar reactions of the balsam with bases are due. The soft resin is, perhaps, formed by oxidation of the volatile oil in the air, and appears to have but a very slight affinity for bases, inasmuch as when isolated it dissolves but slowly, and only, with the aid of heat, in potash and ammonia, forming a turbid solution. (See COPAIBA RESINS.)

Besides these essential constituents, the balsam likewise contains occasionally a small quantity of water, and, according to Durand, small quantities of extractive matter, acetic acid (perhaps also succinic acid), and a fatty substance, which remains behind when the balsam is dissolved in alcohol of specific gravity 0·842; also traces of chloride of calcium. The following are analyses of this variety of copaiba balsam:

	Stoltze.*	Guibourt.†	Gerber.‡ Fresh balsam.	Gerber.‡ Old balsam
Volatile oil	38·00	45·0	41·0	31·97
Alpha-resin	52·75	53·9	51·38	52·68
Beta-resin	1·66	1·1	2·18	11·15
Water and loss	7·59		5·44	4·10
	100·00	100·0	100·00	100·00

II. *Copaiba Balsam, containing only neutral resins.* PARACOPAIBA BALSAM.—This variety, which is of recent introduction, is distinguished from the former by its much greater mobility. In odour and taste it agrees with the preceding, but, according to Posselt (Ann. Ch. Pharm. lxix. 67), behaves in a totally different manner with solvents and with bases. With alcohol, in any proportion, it forms a turbid mixture. Potash and ammonia also form with it turbid liniments, which, when left at rest, deposit the balsam in its original state. It does not thicken with magnesia. The volatile oil, *paracopaiba-oil*, which it yields by distillation with water, is distinguished from the copaiba-oil above-mentioned, by its viscidity, its sparing solubility in absolute alcohol, and especially by not forming a crystalline compound with hydrochloric acid. The resinous cake, brittle in the cold, which remains after the volatile oil has been distilled off, is resolved by cold alcohol into a soluble portion, which separates on evaporation of the alcohol, in drops that gradually solidify in amorphous masses, and another resin, which dissolves only in boiling alcohol and in ether, is difficult to fuse, and likewise uncrystallisable. Neither of these resins exhibits any acid reaction in the state of solution, or forms compounds with bases (see COPAIBA RESINS). One hundred pts. of the Brazilian balsam examined by Posselt, contained 82 pts. of volatile oil, and 18 pts. resin, the greater part of which was soluble in cold alcohol.

The two varieties of copaiba balsam just described, the first of which, from its behaviour with magnesia, is called *solidifiable balsam*, must be regarded merely as types—which are, perhaps, not the only ones—and may vary greatly in the proportion of oil and resin, and therefore in consistence. Oberdörffer (Arch. Pharm. [2] xlv. 172) found in three varieties of mobile copaiba balsam of the first variety:

	I.	II.	III.
Volatile oil	60	58	54
Resins	40	42	46

The following proportions of oil and resin have been found in several balsams of unknown origin:

	Ulex.§	Stockhardt.‖		Procter.¶				
	IV.	V.	VI.	VII.	VIII.	IX.	X.	XI.
Specific gravity	0·928			0·916	0·956	0·983	0·985	0·986
Volatile oil	90	58	56·5	80	65	50	35	34
Resins	11	42	43·5	20	35	50	65	64

The amount of volatile oil was estimated either by the loss of weight which the balsams suffered by boiling with water (I. to VI.), or by continued heating to 120° C. (248° F.), till the weight remained constant (VII. to XI). The balsams IV. to VI. were mobile and are not further distinguished; VII. and VIII. are mobile balsams of the second variety; IX. to XI. viscid balsams of the first variety.

According to Procter, the proportion of oil varies with the age of the trees, the youngest trees yielding the most liquid balsam. The acid resins appear to be formed in the plant itself, while the soft resin (β resin) is produced by the oxidation of the volatile oil, and consequently increases in amount with the age of the balsam, especially when it is kept in loosely closed vessels; this is in accordance with the results of Oberdörffer's analyses just quoted.

Copaiba balsam is used in the preparation of lac-varnishes and tracing paper; but its chief application is in medicine, as a remedy in diseases of the urinary passages. It is not known with certainty to which constituent of the balsam the peculiar physiological action is due; but it does not appear to reside especially in the volatile oil; for in many places, the resin completely freed from oil is successfully used in medical practice, instead of the balsam in its original state. Whether the more oleaginous variety, containing only neutral resins, which is of recent introduction, is capable of exerting the same action as the more viscid and acid variety, which has long been in use, is not yet known.

Copaiba balsam is often adulterated, especially with fixed oils and turpentines. Of

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* Berliner Jahrb. f. Pharm. xxvii. 179.

† Pharm. J. Trans. x. 172.

‡ Brande's Archiv, xxx. 147.

§ Arch. Pharm. cxxii. 14.

‖ Arch. Pharm. xxxviii. 12.

¶ Pharm. J. Trans. x. 603

late years East Indian *wood-oil* (also called *Gurjun balsam*, or *capivi*), which closely resembles copaiba balsam in taste and smell, has been introduced as a substitute for it. This oil may be easily distinguished by its property of becoming gelatinous when heated to 130° C. (268° F.), whereas pure copaiba balsam becomes more fluid when heated.

The presence of fixed oils in copaiba balsam may be detected by the following methods:—1. By placing one or two drops of the balsam on paper, and evaporating it at a very gentle heat. The pure balsam then leaves a hard, sharply defined varnish-like spot, whereas if any fixed oil be present, the spot is soft and surrounded with a circle of fat (Berzelius).—2. The pure balsam, boiled for some hours with water in an open vessel, leaves a resin which becomes brittle on cooling: fixed oils render this residue soft or greasy.—3. The fixed oils remain behind when the balsam is dissolved in 8 pts. of alcohol of 90 per cent. (a smaller quantity of alcohol of that strength would leave some of the balsam undissolved, p. 493). This last method will not indicate the presence of castor-oil, which is itself soluble in alcohol; neither will it detect the presence of less than 10 per cent. of other fixed oils. Turpentine and oil of turpentine may be recognised by their odour, especially when the balsam is dropped upon a metal plate.

All other methods of testing copaiba balsam are founded on the amount of acid resins contained in it, and relate to the first variety (p. 493). This officinal balsam may be regarded as genuine when, besides exhibiting the characters above mentioned (p. 493), it forms a clear or nearly clear solution with alcohol, yields by distillation with water, not more than 45 per cent. of volatile oil; forms a clear solution with $\frac{3}{8}$ of its weight of aqueous ammonia of specific gravity 0·921, and when mixed with $\frac{1}{16}$ of its weight of calcined magnesia, gradually forms (in twenty-four to forty-eight hours) a plastic paste. (Handwört. d. Chem. 2te Aufl. ii. 634.)

Mecca Balsam or Balm of Gilead. *Opobalsamum verum s. gileadense. Baume de la Mecque, de Judée, ou du Caire.*—This balsam is the produce of the *Balsamodendron gileadense* or, *Amyris gileadensis*, a shrub belonging to the terebenthaceous order, native of Arabia Felix. There appear to be three varieties of it. The finest, which is used only in the East, and has a peculiarly fragrant odour, is said to exude from the flowers in clear colourless drops. An inferior sort exudes spontaneously, or from incisions in the young branches of the plant. It is mobile, pale yellow, turbid like almond syrup, has a very agreeable odour like rosemary and lemon, and a bitterish sharp taste. When exposed to the air, it gradually hardens and loses its transparency. The third sort, which is the most common, is obtained by boiling the wood and the branches with water. It is somewhat more viscid than balsam of copaiba, becomes white and soapy when rubbed in the hand, and when dropped upon water, forms a film which is easily removed by a quill feather. Ordinary spirit of wine dissolves it but partially, and leaves a transparent odorous substance, of which warm alcohol of specific gravity 0·815 dissolves about two-thirds. The residue is a flocculent substance, which may be drawn out into threads.

Trommsdorff (Trommsd. Neues Journal, xvi. 62) found in a sample of this balsam, 30 per cent. of volatile oil, 64 per cent. of hard resin, 4 per cent. of soft resin, and 0·4 per cent. of bitter principles. The *volatile oil* was mobile, colourless, fragrant, and had a rough taste; dissolved in alcohol and ether, and with deep red colour in sulphuric acid, whence it was precipitated by water as a resin. It was also resinised by nitric acid. The *hard resin* was honey-yellow, transparent, brittle, of specific gravity 1·333, softened at 44° C., and melted completely at 90°. It dissolved with difficulty in alcohol and ether at ordinary temperatures, easily with aid of heat; it was likewise soluble in oils, both fixed and volatile. It was altered by hot nitric and sulphuric acids, and appeared to combine with alkalis, forming compounds insoluble in free alkali. The *soft resin* was brown and very glutinous, inodorous and tasteless; melted, when dry, at 112° C. It was insoluble in alcohol and ether, but soluble in oils, both fixed and volatile. It was not attacked by alkalis or by strong sulphuric acid; with nitric acid, it swelled up and became friable.

According to Bonastre (Ann. Ch. Pharm. iii. 147), Mecca balsam contains in 100 pts.:

Fragrant volatile oil	10 pts.
Brown bitter extract, soluble in water and alcohol	4 „
Acid resin, soluble in alcohol, and not hardening	70 „
Stiff whitish-grey resin, sparingly soluble in alcohol . . .	12 „
Acid substance and impurities	4 „

Mecca balsam was formerly used in medicine, but has now fallen into disuse on account of its scarcity and dearness. In the East it is used internally as a tonic.

Balsams of the Second Group, containing Cinnamic Acid.

Liquidambar Balsam is the produce of *Liquidambar styraciflua*, a large tree growing in Louisiana, Florida, and Mexico. There are two varieties of it, viz.:

1. *Liquid liquidambar*, or *Oil of liquidambar*, which is obtained by making incisions in the tree, receiving the balsam immediately, in vessels which protect it from the action of the air, and afterwards decanting the liquid from a portion of opaque balsam, which settles to the bottom. It is a thick transparent oil of amber-yellow colour, has an odour like that of liquid storax, but more agreeable, and an aromatic taste, which irritates the throat. It contains a rather large quantity of benzoic or cinnamic acid, and reddens litmus paper strongly. Boiling alcohol dissolves it, with exception of a slight residue, and the filtered liquid becomes turbid on cooling.

2. *Soft* or *white liquidambar* is formed from the preceding by exposure to the air, as when it runs down the stem of the tree and is left there to thicken. It resembles very thick turpentine or soft pitch, is opaque and whitish, has a less powerful and more agreeable odour than the preceding, and a sweet, perfumed, but irritating taste. It contains a large quantity of benzoic or cinnamic acid. By continued exposure to the air, it solidifies completely, and becomes nearly transparent. It was formerly sold as white Peru balsam. (Gerh. iii. 386.)

Peru Balsam. *Balsamum peruvianum; Bals. indicum.*—This balsam is the produce of certain species of *Myroxylum*, or *Myrospermum*, growing on the Balsam coast near San Sonate, in the state of San Salvador, Central America. There are three varieties of it:

1. White Peru balsam.—Obtained from the fruit of the tree by removing the wings and the outer and middle integuments, and subjecting the inner coating, together with the seed, to pressure. The balsam thus obtained is pale yellow, somewhat thick, turbid and granular, and has an agreeable odour of melilot. When left at rest, it deposits a solid crystalline layer. Cold alcohol or ether dissolves it but imperfectly; the same liquids when hot dissolve the greater portion. The alcoholic solution, when left at rest, deposits crystals of myroxocarpin (*q.v.*), of which also the crystalline sediment above mentioned appears to consist. The ethereal extract of the balsam leaves when evaporated a mixture of resin and fixed oil. The balsam distilled with water, yields traces of a volatile oil and a volatile acid (Scharling). According to Guibourt, there is another kind of white Peru balsam, which is identical with liquidambar.

2. Dry Peru balsam, *Balsamum peruvianum siccum*, *Opobalsamum siccum*, is said to be produced from the preceding by hardening in contact with the air. According to Weddell, it exudes spontaneously from the stem of a myroxylum. It is reddish-yellow, translucent, hard, smells aromatic and like vanilla, melts when heated, and burns with a smoky flame; 100 pts. of it contain, according to Tromsdorff, 12 pts. benzoic (more probably cinnamic) acid, 0·2 volatile oil, and 88·0 resin.

3. Black Peru balsam. Black balsam of San Salvador or San Sonate. *Balsamum peruvianum s. indicum nigrum. Baume de Pérou noir.* This, which is the ordinary Peru balsam, has been known in Europe since 1580. It is said to be obtained by making incisions in the stem of the trees, partially detaching a portion of the bark in such a manner as to leave it still connected with the stem at the upper part, then thrusting woollen rags between the bark and the wood, and warming the tree by making a fire round it. Fresh incisions are then made higher and higher up, till the rags are saturated, the process occupying ten or twelve days. The cloths impregnated with balsam are then removed, and well boiled with water, and the balsam which sinks to the bottom is freed from water, which it retains somewhat firmly, by several hours boiling under water. It is then further purified by straining, and sent to Europe by way of Peru, whence its name. (Copious details of the history and preparation of this balsam, are given in *Muspratt's Chemistry*, i. 228; see also *Ure's Dictionary of Arts, Manufactures and Mines*, i. 248.)

Black Peru balsam is viscid but not glutinous, of dark brown colour, opaque in the mass, but in thin layers perfectly transparent, with brown-red colour. Specific gravity 1·15. In contact with the air, it gradually thickens, but does not solidify. It has an agreeable odour, like vanilla, a bitter, persistently irritating taste, and an acid reaction, 1000 parts of the balsam saturating about 75 of carbonate of sodium.

When heated, it takes fire and burns with a smoky flame. When distilled with water, it does not yield any volatile oil, but the distillate contains cinnamic acid, which exists in the balsam in the free state, and may be extracted by repeated boiling with water, or by carbonate of sodium. Peru balsam mixes in all proportions with *absolute alcohol*; but the solution is not quite clear, and deposits a flocculent substance when left at rest. Weaker alcohol dissolves it less easily, and leaves a residue of resin. It is also but incompletely soluble in *ether* and in *oils*, whether fixed or volatile. It mixes without turbidity with ⅛ of its weight of fixed oil, or with ¼ of its weight of balsam of copaiba; but if a larger quantity of either of these liquids be added, two layers are formed. *Sulphuric acid* converts it into a thick red mass, with evolution of sulphurous acid; *nitric acid* acts upon it only when heated, giving off nitrous fumes and hydrocyanic acid; after the evaporation of the mixture, there remains a brownish-yellow bitter substance, soluble in water. When 2 volumes of the balsam are gently heated with 3 volumes of *potash-ley*, of specific gravity 1·3, two layers of liquid are formed, the upper consisting of a brownish oil (oil of Peru balsam), and the lower, which is watery, containing cinnamic acid, resins, and colouring matters in combination with potash. 4 pts. of the balsam form a soapy mixture with 1 pt. hydrate of potassium and 1 pt. of water. When subjected to *dry distillation*, it begins to boil at 287° C. and yields, with continual rise of temperature, an oil coloured by products of decomposition, while a porous charcoal remains in the retort.

Black Peru balsam has been repeatedly analysed. The earliest examination of it was made in 1824, by Stoltze (Berliner. Jahrb. f. Pharm. xxv. 24), who found in 100 pts. 69·0 pts. of a peculiar volatile oil, 6·4 of acid (supposed at the time to be benzoic acid, but really consisting of cinnamic acid), 20·7 resin easily soluble in alcohol, 2·4 resin sparingly soluble in alcohol, 0·6 extractive matter, and 0·9 moisture.

According to Fremy (Ann. Ch. Phys. [2] lxx. 180), the balsam is composed of variable quantities of a volatile oil (*cinnamein* or *styracin*), a crystallisable substance (*metacinnamein*), isomeric therewith, *cinnamic acid*, and *resin*. On dissolving the balsam in alcohol, and adding alcoholic potash, the resin is precipitated in combination with potash, while the cinnamein remains dissolved, and may be precipitated by water, the cinnamic acid still remaining in solution. The oil is purified from resin by solution in rock-oil and evaporation; by exposing it to a low temperature, and redissolving in weak alcohol, the crystalline metacinnamein, which however is not always present, is separated (see CINNAMEIN). The resinous portion of the balsam appears to be a mixture of several distinct resins, one of which agrees in composition with the resin produced from cinnamein by the action of sulphuric acid; another differs from that just mentioned merely by containing a smaller amount of the elements of water. Fremy therefore regards cinnamein and metacinnamein as the original constituents of Peru balsam, the cinnamic acid as a product of oxidation, and the resins as hydrates of cinnamein. This view explains the variation in constitution of the balsam with age; also the fact that cinnamic acid is still present in the balsam after it has been boiled with water, and increases in quantity with the age of the balsam.

For Plantamour's results, which agree with those of Fremy, so far as regards the presence of cinnamein and cinnamic acid, see Ann. Ch. Pharm. xxvii. 329; xxx. 347. According to Scharling (*ibid.* xcvii. 168), the cinnamein obtained from different samples of Peru balsam is not of constant composition; but the formulæ which he assigns to them are improbable.

The resin of Peru balsam mixed with pumice and subjected to dry distillation, yields benzoic acid, together with an oily and a watery distillate. On distilling the former by itself, a lighter oil passes over at 175° C., and afterwards a heavy liquid, which sinks to the bottom. The light oil, repeatedly rectified with potash-ley, and finally over hydrate of potassium, yields pure cinnamene, C^8H^8. The heavier liquid appears to consist of benzoate of methyl and phenic acid: when distilled with potash-ley, it yields wood-spirit. (Scharling, *loc. cit.*)

Black Peru balsam is used in medicine as an application to wounds, and also as an internal remedy. It is also used in perfumery, and in the preparation of chocolate, as a substitute for vanilla. The white and dry balsams (p. 496) are scarce, and have not received any practical application.

Adulterations in Peru balsam may be detected as follows: *Fixed oils* remain undissolved on treating the balsam with strong alcohol; *volatile oils* lower the boiling point, and pass over on distilling the balsam with water; *copaiba balsam* and *turpentine* may be recognised by the odour which they give out when heated; also by yielding volatile oils on distillation with water; *sugar* and all substances soluble in water, by the diminution of volume which the balsam so adulterated undergoes when shaken up with water; syrup of sugar also renders the balsam turbid.

STORAX BALSAM.—This balsam is the produce of *Styrax officinalis*, a shrub growing in the Levant, Palestine, Syria, and Greece. It is imported into Europe from Trieste. There are two principal varieties of it, *Styrax liquidus*, and *Styrax calamita*.

a. *Liquid storax.*—This variety is sometimes transparent, of brownish-yellow colour, of the consistence and tenacity of Venice turpentine, and has a peculiar sweetish or vanilla-like odour; sometimes opaque, with grey colour, the consistence of bird-lime, and a strong oppressive odour, slightly mixed with that of benzene or naphthalene. Liquid storax is a mixture of styrol, cinnamic acid, styracin, and resins.

b. *Reed storax, Styrax calamita.*—This is imported in compact masses of fragrant odour and rich brown colour, interspersed with white tears, whence it has also been called *amygdaloïd storax*. According to Reinsch, it contains about 0·5 per cent of volatile oil, 33 to 54 per cent. resin, 1·1 to 2·6 benzoic acid, 8 to 14 gum and extract, 9·6 to 24 matter extracted by potash, 20 to 27 woody fibre, 5 water, and traces of ammonia. The drug sold under this name is, however, of very variable composition, often consisting of nothing but saw-dust or decayed wood, impregnated with coal-tar, or some similar substance, and bearing no resemblance whatever to the genuine storax.

Storax is used in medicine, as a stimulating expectorant, its operation being analogous to that of Peru balsam or benzoin. It is also used as a detergent, in the form of ointment. (Muspratt's Chemistry, i. 225.)

Tolu Balsam.—This balsam is obtained in large quantity from incisions in the stem of the *Myrospermum toluiferum* (Sprengel), *Myroxylum toluiferum* (Richards), a tree growing in various districts of Columbia, viz. in the mountains of Turbaco and Tolu, and on the Magdalena River. In the fresh state it is yellowish, transparent and liquid, like turpentine (*white tolu-balsam*) but changes rather quickly by keeping, acquiring a reddish-brown colour and stiff consistence (*black tolu-balsam*), and being ultimately converted into a friable substance of granular crystalline structure (*dry tolu-balsam*). It has an aromatic odour, like that of lemon and jasmine, and a sweetish, aromatic, somewhat irritating taste. It melts at a gentle heat; dissolves readily and completely in *alcohol*; less readily in *ether* and in *volatile oils*; not completely in *fixed oils*. Hot *water* extracts from it cinnamic acid (and, according to Deville and Scharling, likewise benzoic acid), together with volatile oil. Heated with strong *sulphuric acid*, it forms a red solution without giving off sulphurous acid. With *potash-ley* of specific gravity 1·17, it forms a clear solution having an odour of violets, and with drops of oil floating on the surface.

Tolu balsam is a mixture of volatile oil, free acid, and resin. The *volatile oil* is obtained by distilling the balsam with water, the quantity being always small, but varying according to the age of the balsam. Deville obtained 0·2 per cent., Scharling 1 per cent., and, by afterwards passing steam heated to 170° C. through the balsam, 0·2 per cent. more. This oil is, according to Deville, a mixture of *tolene*, $C^{12}H^{18}$, passing over betweeen 160° and 170° C., and *cinnamein*, $C^{16}H^{14}O^{2}$, which distils between 340° and 350° C. According to E. Kopp and Scharling, on the other hand, the oil consists wholly of tolene, which, according to Kopp, is isomeric with oil of turpentine, $C^{10}H^{16}$. The small quantity of volatile oil contained in Tolu balsam, and the rapidity with which it hardens by exposure to the air, are characters by which it is readily distinguished from balsam of Peru.

The free acid of Tolu balsam consists, according to Deville and Scharling, of *cinnamic* and *benzoic* acids; according to Fremy and E. Kopp, of cinnamic acid only. The balsam boiled with water, yields a solution which, on cooling, deposits crystals chiefly of cinnamic acid (Deville). The oil obtained by distilling the balsam with water, and cohobating the distillate several times, deposits benzoic acid when exposed to the air (Deville). Benzoic acid is likewise extracted, together with cinnamic acid, by treating the balsam with aqueous carbonate of sodium, or caustic potash, adding chloride of calcium to precipitate the resins, and supersaturating the filtrate with hydrochloric acid (Deville, Scharling). E. Kopp is of opinion that the benzoic acid is a product of decomposition, and does not pre-exist in the balsam.

Resins.—According to E. Kopp, Tolu balsam contains two resins, an α resin, easily soluble in alcohol, and a β resin, $C^{18}H^{20}O^{5}$, sparingly soluble in alcohol.

The α resin, $C^{18}H^{19}O^{4}$, according to Kopp, but more probably $C^{18}H^{18}O^{4}$, as suggested by Gerhardt (Traité, iii. 408), is obtained by treating the balsam with cold alcohol, after it has been freed from volatile oil and cinnamic acid by distillation and boiling with water. It is brown, translucent, and shining; friable in the cold; but the powder cakes together even at + 15° C., and the resin melts at 60° C. Strong sulphuric acid colours it purple-red. When dissolved in potash-ley, and exposed to the air, it oxidises readily, and is converted into β resin. By dry distillation it yields toluene and benzoic acid.

The β resin, $C^{18}H^{20}O^{5}$, is brownish, dull, and without taste or smell; melts at a temperature above 100° C. It is sparingly soluble in alcohol and ether, dissolves with brown colour in potash-ley, and is precipitated with violet colour by sulphuric acid. It is more permanent than the α resin.

The mixture of the two resins, treated with nitric acid, yields a number of volatile and gaseous products, consisting of carbonic anhydride, nitrous anhydride, nitric oxide, bitter-almond oil, hydrocyanic acid, and a small quantity of benzoic acid, and there remains a yellow mass, consisting of benzoic acid and a yellow resinous colouring matter, which prevents the benzoic acid from crystallising till it has been separated by sublimation. The resin thus treated yields about a third of its weight of pure benzoic acid.

According to Deville, Tolu balsam contains only one kind of resin, which has the composition of the β resin just described. To extract it, Deville dissolves the balsam in potash largely diluted with water, saturates the liquid with carbonic acid gas, whereby a small quantity of resin is precipitated, then adds chloride of calcium, which precipitates the carbonic acid and the rest of the resin as calcium-salts, leaving benzoic and cinnamic acids in solution. The rose-coloured mass, left after filtration, is then treated with hydrochloric acid, which dissolves out the lime and leaves the resin, and the latter is purified by solution in a small quantity of alcohol and precipitation by water. It then forms a rose-coloured powder, having a faint odour of vanilla, soluble in alcohol and in potash, very hygrometric, and varying considerably in colour from the effect of atmospheric influences, and perhaps also of light. Treated with fuming nitric acid, it takes fire and burns as in oxygen. By dry distillation, it yields a small quantity of water, benzoic acid, toluol, benzoate of ethyl, and a mixture of carbonic oxide and carbonic anhydride. (Deville.)

Scharling finds that, when the resins of Tolu balsam are mixed with half their weight of powdered pumice, and covered in the retort with a layer of pumice, the process of dry distillation goes on quietly and without tumefaction. 16 pts. of the resin heated in this manner, ultimately to redness, yield 2 pts. of a watery, and 5 pts. of an oily liquid, which is heavier than water, and is resolved by fractional distillation into toluol, phenic acid, and a portion boiling above 198° C. The latter was not obtained of constant boiling point, and yielded by analysis numbers intermediate between the composition of benzoate of ethyl, $C^7H^5(C^2H^5)O^2$, and benzoate of methyl, $C^7H^5(CH^3)O^2$. When distilled with potash, however, it yielded only methylic alcohol, without any common alcohol; hence it appears that the products of distillation of the resins are toluene, phenic acid, and benzoate of methyl.

The mode of formation of Tolu balsam is not known with certainty. If we regard cinnamein as the primary constituent, the resins α and β may be formed from it by absorption of oxygen and water:

$$\underset{\alpha\ \text{resin.}}{C^{18}H^{18}O^4} = \underset{\text{Cinnamein.}}{C^{18}H^{16}O^2} + O + H^2O$$

$$\underset{\beta\ \text{resin.}}{C^{18}H^{20}O^5} = C^{18}H^{16}O^2 + O + 2H^2O$$

or the α resin may be converted by oxidation into the β resin and cinnamic acid:

$$\underset{\alpha\ \text{resin.}}{2C^{18}H^{18}O^4} + O = \underset{\beta\ \text{resin.}}{C^{18}H^{20}O^5} + \underset{\substack{\text{Cinnamic}\\ \text{acid.}}}{2C^9H^8O^2}$$

Lastly, the β resin may split up into benzoic acid, water, and a hydrocarbon:

$$C^{18}H^{20}O^5 = 2C^7H^6O^2 + H^2O + C^4H^6$$

which hydrocarbon is supposed by E. Kopp to give rise to the formation of tolene. Scharling, on the other hand, supposes that all the constituents of the balsam are formed from tolene, inasmuch as this body, when exposed to the air, quickly becomes resinous and acquires an acid reaction. It must be observed, however, that the resins thus formed are very different in composition and properties from those of Tolu balsam, and the nature of the acid has not been determined.

Tolu balsam is used medicinally to facilitate expectoration in coughs and chronic catarrhs; also in perfumery. It is said to be often adulterated with liquid storax, liquidambar, and Canada balsam. Pure Tolu balsam may be known by its perfect transparency when fresh; by its odour; by its freedom from water; by its perfect solubility in potash-ley of 1·17, and in alcohol; and by its reaction with sulphuric acid.

BALSAMS, ARTIFICIAL. Pharmaceutical preparations, chiefly for external use, and somewhat resembling the natural balsams in their physical character, *e. g. Balsamum opodeldoc*, an alcoholic soap-solution containing ammonia; *Balsamum Arcæi*, a salve containing elemi-resin; *Balsamum sulphuris*, a solution of sulphur in linseed oil, &c.

BALTIMORITE. A variety of chrysotil, or fibrous serpentine, found at Baltimore in North America.

BAMLITE. A silicate of aluminium, found in microscopic linear or fibrous crystals, at Bamle in Norway. Specific gravity 2·984; hardness about equal to that of disthene; colour varying from white to pale greenish; lustre vitreous to silky; translucent, or in single individuals nearly transparent and colourless. According to Erdmann's analysis (J. pr. Chem. xxxi. 165) it contains 56·9 silica, 40·73 alumina, 1·04 ferric oxide, 1·04 lime, and traces of fluorine, numbers which correspond nearly to the formula $Si^9Al^{16}O^{30} = 4Al^4O^3.9SiO^2$; but it requires further examination. Kobell regards it as a mixture of disthene and quartz.

BARALITE or **BAVALITE.** A mineral from Baralon, Côte du Nord, containing silica, alumina, ferric oxide, lime, magnesia, and water. It is probably a mixture, the separate constituents of which are not distinguishable by the eye.

BARBATIMAO. A name applied to several Brazilian barks containing tannin, and used both as astringent medicines and in the tanning of leather.

BARDIGLIONE. A blue variety of anhydrite cut and polished for various ornamental purposes.

BAREGIN. *Glairin.*—A nitrogenous substance contained in sulphurous thermal springs, especially in France. It forms a deposit on the sides of the basins and conduits of the springs, which are sometimes filled with water and sometimes empty, never occurring in parts which are constantly full. The name baregin is derived from its occurrence at Barèges; it is also called *Plombierin*, from Plombières, another locality in which it is found in considerable quantity. Baregin is in the moist state a transparent, gelatinous, nearly colourless substance, destitute of taste and odour. It dissolves very sparingly in the cold, more readily at higher temperatures, in water, alcohol, aqueous acids, and alkalis, and in oil of turpentine; insoluble in ether. When dried, it forms a horny mass, and on heating this mass, it emits an odour like that of burnt horn, together with ammoniacal vapours. According to Bouis (Compt. rend. xli. 16) it contains from 44 to 48·7 per cent. of carbon, 6·7 to 7·7 hydrogen, 5·6 to 8·1 nitrogen, and 30·2 to 40·7 per cent. of ash, chiefly consisting of silica. It does not contain sulphur. According to Danberg, it consists for the most part of a mass of confervæ and oscillatoriæ.

Nearly allied to, if not identical with baregin, is a substance which is sometimes formed in the quick method of preparing vinegar (see ACETIC ACID, p. 7), and attaches itself in gelatinous shreds to the inside of the perforated casks. This substance when dried forms a parchment-like layer, containing 42 per cent. carbon and 6 hydrogen, besides nitrogen and oxygen, and leaving an alkaline ash. (Gerh. iv. 536; Handw. d. Chem. 2^{te} Aufl. ii. 643.)

BARILLA or **BARILLOR.** The term given in commerce to the impure soda imported from Spain and the Levant. It is made by burning to ashes different plants that grow on the sea shore, chiefly of the genus *Salsola*, and is imported in hard porous masses of a speckled brown colour. *Kelp*, a still more impure alkali, made in this country by burning various sea-weeds, is sometimes called *British barilla*. These substances were formerly the source of all the soda of commerce; but their use is now almost entirely superseded by the manufacture of soda from common salt.

BARIUM. *Symbol* Ba; *Atomic weight* 68·5.—(The name is derived from βαρύς, heavy, in allusion to the great density of its compounds.) This metal occurs abundantly as a sulphate and carbonate; also in the mineral *barytocalcite*, a carbonate of barium and calcium, in certain ores of manganese, in Harmotome and in Brewsterite; traces of it has also been found in mineral waters. It is never found native. The oxide, *baryta*, was first recognised as a peculiar earth, distinct from lime, by Scheele, in 1774; and the metal itself was first obtained by Davy, in 1808.

Preparation.—1. Hydrate of barium, or the carbonate, chloride, or nitrate, is made into a doughy mass with water, formed into a cup, and placed upon a platinum dish, which is connected with the positive pole of a voltaic battery of 500 pairs of plates, the cup being filled with mercury, into which the negative wire dips. The amalgam of barium thus obtained is heated in a tube of glass without lead, filled with the vapour of rock-oil, till all the mercury is sublimed (Sir H. Davy). If the hydrate of barium is mixed with oxide of mercury, the amalgam is obtained in larger quantity (Sir H. Davy.) Hare (J. pr. Chem. xix. 249) prepared the amalgam in a similar manner from moistened chloride of barium surrounded by a freezing mixture, using two batteries, each of 100 pairs, and containing more than 100 square feet of zinc. The mercury was expelled by heating the amalgam in an iron crucible provided with an iron cover, and exhausted of air.—2. Barium may be obtained in an impure state, according to Davy, by passing vapour of potassium over red-hot baryta or chloride of barium.—3. Pure baryta or the nitrate is placed in a hole made in a piece of charcoal or slate, and exposed to a burning jet of detonating gas, produced from three measures of hydrogen and one measure of oxygen gas. Effervescence takes place, and white, shining little globules of metallic barium are formed. The baryta must be anhydrous and the detonating gas must be passed through oil and not through water; otherwise a translucent vitreous or horny mass will be obtained. (Clarke, Ann. Phil. xvii. 419.)—4. Bunsen subjects chloride of barium, mixed up to a paste with water and a little hydrochloric acid, at a temperature of 100° C., to the action of the electric current, using an amalgamated platinum wire as the negative pole. In this manner, the metal is obtained as a solid, silver-white highly crystalline amalgam, which, when placed in a little boat made of thoroughly ignited charcoal, and heated in a stream of hydrogen, yields barium in the form of a tumefied mass, tarnished on the surface, but often exhibiting a silver-white lustre in the cavities (Pogg. Ann. xci. 619). Matthiessen has obtained barium by a method similar to that adopted for strontium (*q. v.*); but only in the form of a metallic powder.

Properties.—Barium, according to Davy, is a silver-white metal with less lustre than cast-iron; according to Clarke, it has the colour and lustre of iron; according to Matthiessen, it is a yellow powder. It sinks rapidly in strong sulphuric acid, even when surrounded by bubbles of gas. Its specific gravity, according to Clarke, is 4·0 or somewhat greater. It is ductile, and may be beaten flat, though with difficulty. It melts below redness, and does not volatilise at a red heat. It oxidises rapidly in the air, becoming heated at the same time, and decomposes water rapidly at ordinary temperatures. When heated in the air, it burns with a dark red light (Davy); before the oxy-hydrogen blowpipe it burns with a greenish flame (Clarke). Sulphuric acid rapidly converts it into sulphate, with evolution of hydrogen.

BARIUM, BROMIDE OF. $BaBr$. *Crystallised:* $BaBr.H^2O$.—Prepared by saturating baryta-water, or sulphide, or carbonate of barium with hydrobromic acid, or by decomposing the sulphide with free bromine, sulphur being at the same time precipitated. It is very soluble in water and crystallises with difficulty. Isomorphous with the chloride. It is soluble in strong alcohol, and may thus be separated from the chloride, which is nearly insoluble in that liquid.

BARIUM, CHLORIDE OF. $BaCl$. *Crystallised*, $BaCl.H^2O$.—The hydrated salt was formerly called *Terra ponderosa salita.* This salt is prepared either from the carbonate or from the sulphate of barium, both of which are natural minerals. The carbonate (witherite) is simply dissolved in hydrochloric acid, and the resulting chloride purified by recrystillation. From the native sulphate (heavy spar), the chloride may be prepared in two ways: 1. By igniting the sulphate in a crucible with pounded coal, whereby it is converted into sulphide, Ba^2S, extracting the sulphide by boiling water, and decomposing the filtered solution with hydrochloric acid:

$$Ba^2S + 2HCl = 2BaCl + H^2S;$$

The acid is added in sufficient quantity to produce a strong acid reaction, and the liquid is boiled for some time to drive off all the sulphuretted hydrogen, then filtered, evaporated, and cooled till it crystallises.—2. By heating a mixture of 2 pts. heavy spar, and 1 pt. fused chloride of calcium to redness for about an hour. Sulphate of calcium and chloride of barium are then formed ($SO^4Ba^2 + 2CaCl = SO^4Ca^2 + 2BaCl$), and the latter may be extracted by pulverising the fused mass, boiling with water, and filtering as quickly as possible; otherwise, a portion of the chloride of barium will be reconverted into sulphate, because the sulphate of calcium in the residue gradually dissolves in the water, and mixing with the dissolved chloride of barium, produces a reaction exactly the reverse of that which took place in the fused mass. The decomposition of the sulphate may be facilitated by adding to the mixture in the crucible a quantity of iron filings and charcoal. Sulphide of iron is then formed, together with an insoluble oxysulphide of calcium, from which the chloride of barium may be separated by water as above.

Commercial chloride of barium often contains small quantities of the chlorides of strontium and calcium; also chloride of aluminium, sesquichloride of iron, and sometimes traces of copper and lead. The chlorides of strontium and calcium may be removed by washing the crystals with alcohol; the latter also by digesting the aqueous solution with carbonate of barium, whereby the chloride of calcium is slowly decomposed and converted into carbonate; the same decomposition may be more quickly effected by adding baryta-water, and then passing carbonic acid gas into the liquid. Digestion with carbonate of barium also precipitates the aluminium and iron in the form of sesquioxides. Lead and copper may be precipitated by adding to the solution a small quantity of sulphide of barium.

Chloride of barium crystallises from its aqueous solution in transparent, colourless, four-sided tables, belonging to the trimetric or right prismatic system. The form of the crystals resembles that of heavy spar. The angles are $\infty P : \infty P = 93° 20'$; $oP : \frac{1}{3}\bar{P}\infty = 142° 35'$; $oP : \frac{1}{2}\bar{P}\infty = 140° 57'$. The crystals decrepitate in the fire. Their specific gravity is 2·66 (Filhol); cubical expansion from 0° to 100° C. = 0·00987 (Joule and Playfair). They have an unpleasant, bitter, and sharply saline taste, excite nausea, and are highly poisonous.

100 pts. of water at 0° C. dissolve 32·62 pts. of anhydrous chloride of barium, and

0·2711 pts. for every degree above 0° C.; 100 pts. of water at 15·6 dissolve 43·5, and at 105·5°, 78 pts. of the crystallised chloride (Gay-Lussac). One pt. of crystallised chloride of barium dissolves at 18·1° in 2·257 pts. of water, forming a solution of specific gravity 1·28251 (Karsten). Specific gravity of a saturated solution at 8° = 1·270 (Anthon). Water acidulated with hydrochloric acid dissolves less than pure water, and concentrated aqueous hydrochloric acid hardly any; so that a saturated solution in water is precipitated by it. Hot absolute alcohol dissolves only $\frac{1}{400}$ pt. of the crystals, but more if it contains water. According to Fresenius (Ann. Ch. Pharm. lix. 117), one pt. of the salt dissolves in 8108 pts. of alcohol of 99·3 per cent. at 14° C., and in 4857 pts. of the same alcohol at the boiling heat.

The crystals do not effloresce in the air: at 100° C. they give off the whole of their water, leaving the anhydrous chloride in the form of a white mass, which melts at a full red heat, and is translucent after solidification. Specific gravity of the anhydrous chloride = 3·7037 (Karsten), 3·8 (Richter), 3·86 to 4·156 (Pol. Boullay). Heated by itself, it does not become alkaline till after fusion; but when heated in aqueous vapour, it becomes alkaline below the melting point, and evolves hydrochloric acid. By ignition with sulphur it is partly changed into sulphide of barium (Karsten). It is not decomposed, at ordinary temperatures, by vapour of anhydrous sulphuric acid. According to H. Wurtz, it completely decomposes silicates when fused with them.

Chloride of barium in the state of concentrated solution, is decomposed by nitrate of potassium or sodium, yielding nitrate of barium and a chloride of the alkali-metal. It forms a crystalline compound with glycocol. Blood mixed with it remains fluid and does not putrefy.

The chief use of chloride of barium is as a chemical reagent, especially for the detection and estimation of sulphuric acid.

BARIUM, CYANIDE OF. See Cyanides.

BARIUM, DETECTION AND ESTIMATION OF. 1. *Reactions in the dry way.*—Barium-compounds, heated in the inner blowpipe flame, colour the outer flame green. They likewise impart a green colour to the flame of alcohol, and when this flame is examined with a prism by Bunsen and Kirchhoff's method (see Analysis, Inorganic, p. 214, and Light), a spectrum is seen, having several broad green bands, in the neighbourhood of Fraunhofer's lines *b*, *E*, a bright yellow band coincident with the line *D*, a bright orange band just beyond it, and two fainter orange-red bands, one of which nearly coincides with the line *C*.

Reactions in the wet way.—The hydrate, sulphide, chloride, nitrate, and many organic salts of barium, the acetate, for example, are soluble in water; most of the other salts are insoluble in water, but soluble in nitric and hydrochloric acid: the sulphate and the silicofluoride are insoluble in all acids. All barium-compounds are colourless, excepting those which, like the chromate, contain a coloured acid. The soluble salts of barium are poisonous. Solution of *potash* (free from carbonate), forms a precipitate of hydrate of barium, only in very concentrated solutions of barium-salts. *ammonia* forms no precipitate, even in the most concentrated solutions. *Alkaline carbonates* form a white precipitate of carbonate of barium, soluble, with efflorescence, in hydrochloric acid. *Phosphate*, *arsenate*, *borate*, and *iodate of sodium*, also form precipitates soluble in acids. *Free oxalic acid*, or acid *oxalate of potassium*, precipitates oxalate of barium, only from very concentrated solutions; neutral alkaline oxalates form a precipitate in all neutral solutions of barium-salts, which are not very dilute. *Neutral alkaline succinates* precipitate barium-salts quickly or slowly, according to the concentration of the solutions. *Ferrocyanide of potassium* forms a precipitate in moderately dilute solutions; *ferricyanide* only in strong solutions. *Sulphydric* acid, *sulphide of ammonium*, and *perchloric acid*, form no precipitates. *Sulphuric acid* and *soluble sulphates*, throw down sulphate of barium, from all solutions of barium-salts, whether neutral or acid. The precipitate is insoluble in nitric or hydrochloric acid, even at the boiling heat. A solution of nitrate of barium, containing only 1 pt. of baryta in 50,000 to 100,000 pts. of water, gives a very distinct cloudiness with sulphuric acid or sulphate of sodium; with 200,000 to 400,000 pts. of water, after some minutes only; and with 800,000 pts. of water, the reaction is no longer visible. (Lassaigne, J. Chim. méd. viii. 526.) According to Harting (J. pr. Chem. xxii. 58), a solution of chloride of barium containing 1 pt. of baryta in 71,000 pts. of water, becomes turbid with sulphate of sodium after the lapse of half an hour. Alkaline *chromates* form with barium-salts, a yellowish precipitate of chromate of barium, insoluble in dilute acids, soluble only in a large excess of nitric acid. *Hydrofluosilicic* acid forms with barium-salts, after a while, a white crystalline precipitate, nearly insoluble in nitric or hydrochloric acid. This reaction will detect 1 pt. of the chloride in 3800 pts. of water. The precipitation is accelerated by addition of alcohol.

This last reaction affords a complete distinction between barium and strontium;

the latter metal not being precipitated by hydrofluosilicic acid. The reaction with sulphuric acid distinguishes barium in solution from all other metals, except lead and strontium. From lead it is easily distinguished by its behaviour with sulphuretted hydrogen, which forms a black precipitate with lead, and by many other characters. Strontium and calcium are distinguished from barium by the greater solubility of their sulphates, so that a solution of sulphate of strontium, or calcium, added to a soluble barium-salt, forms a precipitate of sulphate of barium. Another distinction is afforded by the colour imparted to the flame of alcohol by the compounds of these two metals, barium-compounds colouring the flame pale green (p. 500), while strontium compounds colour it deep red. The tabular crystals of chloride of barium, which are nearly insoluble in alcohol, likewise afford a means of distinguishing barium from strontium and calcium, the chlorides of which form hygroscopic needle-shaped crystals, easily soluble in alcohol.

3. *Quantitative Estimation.*—Barium is always estimated in the form of sulphate. The precipitation is effected by means of dilute sulphuric acid. The acid must be added in excess, and to a hot solution of the barium-salt; otherwise a small quantity of the original salt, especially if it be nitrate, will be thrown down undecomposed together with the sulphate. The precipitate is washed with hot water, ignited at a moderate heat, together with the filter, and the amount of barium or of baryta calculated from its weight. 100 pts. of it correspond to 58·78 pts. of barium, and 65·64 of baryta.

This mode of estimating barium is very exact; but the precipitate, unless certain precautions are taken, is very troublesome to filter, sometimes passing through as a milky liquid, and sometimes completely stopping up the pores of the paper. To avoid these inconveniencies, the liquid must be heated, and the precipitate allowed to settle down completely, before the filtration is commenced. The clear liquid is then to be passed through the filter, the precipitate stirred up with boiling water, and again left to settle down, this clear liquid also poured through the filter, and the same process repeated three or four times. The result of this treatment is to render the precipitate dense and granular; it may then be poured on the filter, and washed with hot water as above-mentioned.

Recent experiments have shown that sulphate of barium is soluble to a perceptible extent in strong hydrochloric, and still more in nitric acid (Calvert, Chem. Gaz. 1856, 55.—Nicholson and Price, Phil. Mag. [4] xi. 169.—Noad, Chem. Soc. Qu. J. ix. 25). According to Seigle (J. pr. Chem. lxix. 144), it is also slightly soluble in dilute acids, but less in acetic than in hydrochloric or nitric acid. Care must therefore be taken that the liquid, from which the sulphate of barium is precipitated, does not contain too much free acid; and it must be washed with pure, not with acidulated water.

Barium may also be estimated as carbonate; but the method is less accurate than that just described, because carbonate of barium is not completely insoluble in water.

4. *Atomic Weight of Barium.*—The most exact estimations of this number have been made by determining the amount of chloride of silver obtained by precipitating pure chloride of barium with nitrate of silver. In this manner Marignac (Ann. Chem. Pharm. lxviii. 215), operating on chloride of barium purified by washing with alcohol, recrystallisation from water, and drying at a low red heat, found, as a mean of six closely agreeing experiments, that 1 pt. of silver corresponds to 0·96365 pt. of BaCl. Hence, the atomic weight of silver being 108, we have:

$$\begin{array}{lcl} \text{Atomic weight of BaCl} = 0{\cdot}96365 \times 108 & = & 104{\cdot}07 \\ \text{Whence deducting} \quad . \quad \text{Cl} \quad . \quad . & = & \underline{35{\cdot}50} \\ \text{There remains} \quad . \quad . \quad \text{Ba} \quad . \quad . & = & 68{\cdot}57 \end{array}$$

In like manner, the atomic weight of barium was estimated by Berzelius (Schw. J. xx. 1014) at 68·40, and by Pelouze (Compt. rend. xx. 1047) at 68·65.

Lastly, Dumas (Ann. Ch. Phys. [3] lv. 129), by numerous experiments made with chloride of barium, carefully purified and fused in a stream of hydrochloric acid gas, has obtained results varying between the limits 68·47 and 68·56; mean value = 68·5, which last number is here adopted.

The atomic weight of barium has likewise been estimated from the amount of sulphate produced from a given weight of chloride; but the results do not appear to be so trustworthy as those obtained by the method above described.

5. *Separation of Barium from other metals.*—The precipitation of barium by sulphuric acid affords the means of separating it from all other elements excepting strontium, calcium and lead. From *strontium* and *calcium* it may be separated by hydrofluosilicic acid, which throws down a crystalline precipitate of silicofluoride of

barium $2BaF.SiF^2$. This precipitate is somewhat soluble in water, but the separation may be rendered complete by adding alcohol and warming the liquid: from dilute solutions it takes some time to settle down. It must be collected on a weighed filter, dried at a moderate heat, and weighed. 100 pts. of it correspond to 49·01 of barium and 54·73 of baryta. For other methods of separation, see Calcium and Strontium.

The separation of *lead* from barium is easily effected by sulphydric acid, which precipitates the lead as sulphide.

BARIUM, FLUORIDE OF. BaF.—Obtained by neutralising baryta-water with hydrofluoric acid, by digesting the recently precipitated carbonate in that acid, or by decomposing nitrate of barium with fluoride of potassium or sodium. It is a white powder, or, when obtained by evaporating the acid solution, a granular crystalline crust. It is insoluble in water, but dissolves easily in nitric, hydrochloric, or hydrofluoric acid.

Fluoride of barium unites with the fluorides of boron and silicon, forming the compounds $BaF.BF^3$ and $2BaF.SiF^2$. The latter is nearly insoluble in water, and serves for the separation of barium from strontium and calcium, p. 502 (see Borofluorides and Silicofluorides). It also forms a crystalline compound with chloride of barium, BaCl.BaF, which is produced on mixing a solution of fluoride of potassium or fluoride of sodium with chloride of barium. This compound is more soluble than the fluoride itself, and remains as a granular mass when the solution is evaporated.

BARIUM, IODIDE OF. BaI.—Formed when hydriodic acid gas is passed over baryta at a red heat, the combination being attended with production of light. Protosulphide of barium dissolved in water is mixed with a saturated alcoholic solution of iodine [iodine without the alcohol might be preferable], as long as a precipitate of sulphur is formed; the colourless filtrate is boiled rapidly—so as to prevent the action of the air—almost to dryness; the mass is dissolved in a small quantity of water, and filtered quickly; and the filtrate is evaporated to dryness in as short a space of time as possible in a glass bolt-head. (O. Henry.)

On redissolving the mass in hot water and leaving the solution to cool, the hydrated salt crystallises in slender deliquescent needles containing, according to Croft (Chem. Gaz. 1856, p. 125), $2BaI.7H^2O$; they dissolve readily in alcohol. Heated out of contact with the air, they leave the anhydrous salt, which is not decomposed by heat in a close vessel, but in contact with the air, decomposes slowly at ordinary temperatures and quickly when heated, giving off vapours of iodine and leaving baryta.

BARIUM, OXIDES OF. Barium forms two oxides, a protoxide, Ba^2O, and a dioxide or peroxide, BaO; the first produced by the direct oxidation of the metal, or by heating certain of its salts; the second, by heating the protoxide to dull redness in contact with excess of oxygen.

Protoxide of Barium, or Baryta, Ba^2O, or *BaO*. *Barytes*, *Terra ponderosa*, *Terre pésante*, *Schwererde*.—Barium oxidises rapidly in the air, even at ordinary temperatures, and when heated, burns with a dark-red light and is completely converted into anhydrous baryta. This oxide is however more readily obtained by igniting the nitrate or carbonate of barium.

Preparation.—1. Nitrate of barium is heated in a porcelain crucible, or better in a porcelain retort, till it is completely decomposed, and no more red vapour or free oxygen is given off. The heat should be moderate at first, because the nitrate fuses and froths very much; but towards the end of the process, it must be raised to bright redness. If the heat is too long continued, the baryta is apt to absorb carbonic acid and oxygen from the fire.

It is not convenient to use a platinum crucible in this process, because baryta attacks platinum rather strongly at high temperatures, and if a Cornish or Hessian crucible be used, the baryta becomes contaminated with silica, alumina, oxide of iron, and other matters derived from the crucible. A porcelain vessel is attacked in the same manner, though less strongly, and the baryta prepared in it always contains small quantities of alumina and silica. This contamination, and likewise the inconvenience arising from the frothing of the mass, may be obviated in some cases by mixing the nitrate with rather more than its own weight of pounded sulphate of barium (heavy spar). Such a mixture does not fuse, and may therefore be heated in an earthen crucible without attacking it (Mohr, Ann. Ch. Pharm. xxvii. 27). This process is very convenient when the baryta is to be used for purposes for which the presence of the sulphate is not objectionable, as for preparing baryta-water or the hydrate.

2. On the small scale, baryta may be conveniently prepared by igniting the iodate of barium, which readily gives up all its iodine and $\frac{5}{6}$ of its oxygen without fusion or frothing ($2IO^3Ba = Ba^2O + I^2O^5$).—3. Carbonate of barium exposed to the strongest heat of a forge-fire is converted into baryta (Abich), and at an ordinary white heat, when mixed with $\frac{1}{10}$ of its weight of lamp-black or charcoal, and made into a thick

paste with oil; the mixture should be heated in an earthen crucible lined with lampblack, and having a close-fitting cover. Baryta is prepared by this process on the large scale from Witherite, to be used in separating crystallised sugar from molasses (Leplay and Dubrunfaut, Sill. Am. J. [2] xvi. 276). Baryta is also prepared on the large scale by igniting a mixture of the carbonates of barium and calcium in a current of aqueous vapour. (Jacquelain, Compt. rend. xxxii. 877.)

Properties.—Greyish-white, friable mass, of specific gravity 4·7 (Karsten); 5·54. (Filhol). It is strongly alkaline, caustic, and poisonous. It melts only at the strongest heat of a forge-fire, or in the flame of the oxyhydrogen blowpipe, forming a lead-grey slag. It is a non-conductor of electricity, but may be decomposed by the electric current, with the intervention of mercury, yielding barium and oxygen (p. 560). Potassium deoxidises it at a red heat. Heated in vapour of sulphide of carbon, it forms carbonate and sulphide of barium:

$$3Ba^2O + CS^2 = CO^3Ba^2 + 2Ba^2S.$$

With water, it forms a hydrate (see below). It unites with alcohol and wood-spirit, forming the compounds $Ba^2O.2C^2H^6O$ and $Ba^2O.2CH^4O$. It dissolves readily in dilute nitric and hydrochloric acid, and in some other acids; with many acids, it forms insoluble salts. When vapour of sulphuric anhydride is passed over baryta, heated to low redness in a glass tube, combination takes place attended with incandescence, and sulphate of barium, SO^4Ba^2, is produced.

OXIDE OF BARIUM and HYDROGEN; HYDRATE OF BARIUM, BaHO or *BaO.HO*. *Hydrate of Baryta, Caustic Baryta, Hydrated oxide of Barium.*—Formed by the action of water on anhydrous baryta ($Ba^2O + H^2O = 2BaHO$). When anhydrous baryta is sprinkled with water, the hydration takes place, with great evolution of heat and expansion of volume. Anhydrous baryta also rapidly absorbs water from the air. The hydrate is usually prepared by heating a solution of sulphide of barium (obtained by igniting the native sulphate with coal or charcoal) with oxide of copper, till a filtered portion of the liquid gives a white instead of a black precipitate with lead-salts.—Another mode of preparation is to decompose the nitrate of barium with caustic soda. A solution of soda of specific gravity 1·10 to 1·15, whose strength has been previously determined, is mixed with an equivalent quantity of finely pounded nitrate of barium, the liquid being kept in a state of ebullition, and water being added from time to time in small portions to facilitate the solution of the nitrate; and when the whole is dissolved, the boiling liquid is rapidly filtered, if necessary, through a folded filter into a bottle which can be well closed. On cooling, it deposits an abundant crop of crystals of the hydrate, which may be freed from the mother-liquor by draining, or better by means of a centrifugal machine. The crystals retain but a very small quantity of nitrate, and may be freed from it by recrystallisation. Chloride of barium may also be used in this preparation, instead of the nitrate, but the presence of small quantities of chloride of sodium in the product is more likely to be detrimental in the use of the baryta, than that of the nitrate. (Mohr, Arch. Pharm. [2] lxxxviii. 38.)

Hydrate of barium crystallises from its aqueous solution in transparent, colourless, four or six-sided prisms with four-sided summits. They contain 4 at. water: $BaHO.4H^2O$; dissolve in 20 pts. of water at 15° C. and in 2 pts. of boiling water. The aqueous solution, Baryta-water, has a strong alkaline reaction, is highly caustic, and rapidly absorbs carbonic acid from the air, forming a film of carbonate on the surface. The crystals are efflorescent, and in vacuo over oil of vitriol, give off $\frac{7}{8}$ of their water of crystallisation, leaving $2BaHO.H^2O$. At 100° C. they melt, giving off 1 at. water, and at a red heat, the remainder of the water of crystallisation is given off, leaving the pure hydrate BaHO (Bloxam, Chem. Soc. Qu. J. xiii. 49). This, when heated alone, is not reduced to anhydrous baryta below a red heat, but when heated in a stream of carbonic anhydride, it is easily converted into carbonate of barium, with elimination of water:

$$2BaHO + CO^2 = CO^3Ba^2 + H^2O.$$

Heated in a current of air, it takes up oxygen and is converted into peroxide of barium, also with elimination of water. (Boussingault.)

$$2BaHO + O = 2BaO + H^2O.$$

Hydrate of barium is extensively used as a chemical reagent, viz. for the estimation of carbonic acid, for precipitating metallic oxides, and especially for separating magnesia from the alkalis.

PEROXIDE OF BARIUM, BaO or *BaO²*.—Produced by heating anhydrous baryta or hydrate of barium to low redness in a current of pure oxygen, or of air free from carbonic acid. Pure anhydrous baryta absorbs oxygen with facility; the hydrate less readily, because it melts at the temperature required for the absorption;

the absorption may however be rendered rapid by mixing the hydrate of barium with lime and magnesia in sufficient quantity to prevent fusion, and keeping the mass in a porous state, so that the oxygen may penetrate it thoroughly. Peroxide of barium may also be produced by sprinkling red-hot baryta with four times its weight of pounded chlorate of potassium in successive small portions. Chloride of potassium is formed at the same time, and on washing out this salt with water, the peroxide remains in the form of a hydrate.

Peroxide of barium is a grey powder, somewhat more fusible than anhydrous baryta. At a strong red heat, it evolves oxygen and is converted into baryta, and when vapour of water is passed over it at a red heat, it likewise gives up half its oxygen and is converted into hydrate of barium. The absorption of oxygen by hydrate of barium at a red heat, and its subsequent evolution when the resulting peroxide is heated in a stream of aqueous vapour, has been proposed by (Boussingault, Ann. Ch. Phys. [3] xxx. 5) as a means of extracting oxygen from the air by a continuous process. Hydrate of barium mixed with lime and magnesia, as above described, is heated in a porcelain tube through which a current of air previously freed from carbonic acid is drawn by an aspirator: and as soon as the conversion of the hydrate into peroxide is complete, the current of air is stopped, the temperature is raised, and vapour of water is passed through the tube as long as oxygen continues to be given off. Anhydrous baryta may also be used instead of the hydrate, being first converted into peroxide as above, and the peroxide then decomposed by heating it to bright redness without passing aqueous vapour over it: but the temperature required for this decomposition is much higher; and moreover if the baryta contains small quantities of silica and alumina, which is often the case, it cakes into a very hard mass after frequent exposure to a high temperature, and will then no longer absorb oxygen with facility.

Peroxide of barium is readily decomposed by carbon, phosphorus, sulphur, hydrogen, and the metals, at a red heat, and by sulphydric acid at ordinary temperatures. Heated over a large spirit-lamp in a rapid current of carbonic oxide, it becomes white-hot, and at the same time small white flames burst out from its surface, probably arising from the evolution of oxygen from the still undecomposed peroxide. A similar but more brilliant appearance is presented when the peroxide is heated in sulphurous anhydride (Wöhler, Ann. Ch. Pharm. lxxxviii. 125). In contact with strong sulphuric acid, it gives off oxygen at ordinary temperatures or when gently heated. If the temperature of the mixture does not exceed 50° or 60° C., part of the oxygen is evolved in the form of ozone; but above 70° C., nothing but ordinary oxygen is evolved.

Peroxide of barium thrown into water diffuses itself through the liquid and forms a hydrate, probably containing $BaO.3H^2O$. The same hydrate is precipitated in crystalline scales when peroxide of hydrogen is added to strong baryta-water; it is slightly soluble in cold water, but decomposes at the boiling heat, yielding free oxygen and hydrate of barium.

Both the anhydrous peroxide and the hydrate dissolve in excess of water acidulated with hydrochloric acid, forming chloride of barium and peroxide of hydrogen, without evolution of oxygen ($BaO + HCl = BaCl + HO$). When the peroxide is mixed with acidulated water in presence of oxide of silver, peroxide of manganese, peroxide of lead, &c., oxygen is evolved, both from the peroxide of barium and from the other oxide, so that the peroxide of barium here acts as a reducing agent (see CHEMICAL AFFINITY and PEROXIDE OF HYDROGEN). Oxide, chloride, sulphate, or carbonate of silver, introduced into an acid solution of peroxide of barium, is partly reduced to metallic silver, the quantity thus reduced being, however, always less than that which is equivalent to half the oxygen in the peroxide of barium ($Ba^2O.O$). The quantity reduced increases with the amount of silver-salt present, and diminishes as the temperature is higher. A small quantity of the silver-compound, or of any similar substance, is capable of decomposing a large quantity of peroxide of barium. Iodine, on the other hand, decomposes an exactly equivalent quantity: $BaO + I = BaI + O$. (Brodie, Phil. Trans. 1850, 759.)

BARIUM, OXYGEN-SALTS OF. The general characters and reactions are described at p. 502. For the special descriptions, see the several ACIDS.

BARIUM, OXYSULPHIDES OF. A solution of sulphide of barium in boiling water, left to stand in a close vessel, first deposits crystals of hydrate of barium, and the liquid decanted therefrom yields scaly crystals, whose composition is nearly expressed by the formula $Ba^{14}S^2O^4.58H^2O$, and afterwards granular crystals, consisting of $Ba^4SO.10H^2O$. A moderately concentrated solution of the sulphide deposits, after about two months, large transparent tabular crystals, having the form of a hexagonal dodecahedron, with truncated summits, and containing $Ba^8S^3O.28H^2O$, or $Ba^2O.10H^2O + 3(Ba^2S.6H^2O)$ (H. Rose). These oxysulphides are very easily decomposible, being resolved by hot water into hydrate and sulphydrate of barium, of which, perhaps, they are merely mixtures.

BARIUM, PHOSPHIDE OF. BaP?—When vapour of phosphorus is passed over red hot baryta, a brownish-red mixture of phosphide and phosphate of barium is obtained, commonly called *phosphuret of baryta*, the reaction perhaps taking place in the manner represented by the equation:

$$4Ba^2O + 6P = 5BaP + PO^4Ba^3.$$

It is decomposed by water, forming a solution of hypophosphite of barium, and giving off a mixture of spontaneously inflammable phosphoretted hydrogen gas and free hydrogen.

BARIUM, SELENIDE OF. Ba^2Se, or *BaSe*.—Produced by exposing selenite of barium to a red heat in contact with hydrogen gas or finely divided charcoal (lamp-black). It is soluble in water, but decomposes at the same time, like the monosulphide, yielding hydrate of barium, and a higher selenide of barium, the solution of which is decomposed by acids, with evolution of selenhydric acid and precipitation of selenium.

BARIUM, SULPHIDES OF. The *protosulphide*, Ba^2S, or *BaS*, is obtained by passing sulphydric acid or vapour of sulphide of carbon over red-hot baryta, or by reducing pulverised sulphate of barium in a stream of hydrogen or carburetted hydrogen. Either of these processes yields a very pure product; but for preparation on the larger scale, the native sulphate of barium is heated to bright redness with carbonaceous matter. If charcoal is used, it must be thoroughly well incorporated with the heavy spar, otherwise the reduction will be imperfect, as no fusion takes place. The admixture of resin, oil, or starch is advantageous, to bind the mass together and produce partial fusion; but a much better method is to mix the powdered sulphate with about $\frac{1}{8}$ of its weight of bituminous coal, and heat the mixture in a crucible to full redness for an hour; the tarry matter of the coal then penetrates thoroughly into the mass, so that every particle of the sulphate comes well in contact with the reducing matter.

The mass thus obtained consists of sulphide of barium mixed with excess of carbonaceous matter and undecomposed sulphate; the sulphide of barium may be extracted by treating the mass with a sufficient quantity of hot water, and crystallised. Another method is to ignite a mixture of 100 pts. heavy spar, 200 common salt, and 15 pts. charcoal powder in a reverberatory furnace, and extract the sulphide of barium by hot water. The use of the chloride of sodium is to promote fusion. (Kuczinski, Repertory of Patent Inventions, 1835, p. 151.)

Pure sulphide of barium is a white mass, having a hepatic odour and alkaline taste, and easily soluble in water. Exposed to the air, it absorbs water and carbonic acid, and is converted into carbonate, with evolution of sulphuretted hydrogen. When heated in the air, it oxidises but slowly, but when heated to redness in an atmosphere of aqueous vapour, it is converted into sulphate of barium, with elimination of hydrogen.

Sulphide of barium dissolved in water is easily decomposed by boiling with *oxide of copper, oxide of iron, &c.*, forming hydrate of barium and sulphide of copper, &c. *Hydrochloric, nitric, carbonic acid, &c.* decompose it, eliminating sulphuretted hydrogen, and forming chloride, nitrate, &c. of barium. *Chlorine, bromine* and *iodine* decompose it, with formation of the corresponding salts and deposition of sulphur. Sulphide of barium is indeed the material most generally used for preparing the other compounds of barium.

A mixture of sulphide of barium with the sulphate, such as is obtained by igniting the sulphate with an insufficient quantity of carbonaceous matter (gum-tragacanth answers well, because it forms a paste with the heavy spar), acquires by exposure to the sun's rays the property of shining in the dark: it is called the *Bolognian phosphorus.*

With *water*, protosulphide of barium forms hydrate and sulphydrate of barium:

$$Ba^2S + H^2O = BaHO + BaHS.$$

The quantity thus decomposed varies with the quantity and temperature of the water. When crude sulphide of barium, prepared by igniting the sulphate with carbonaceous matter, is treated nine times in succession with a quantity of cold water less than sufficient to dissolve the whole, the mass being digested for twenty-four hours each time in a closed vessel, the first two solutions obtained are of a pale yellow colour; yield a large quantity of sulphuretted hydrogen and a precipitate of sulphur, when treated with hydrochloric acid; and form with chloride of manganese, a flesh-coloured precipitate of sulphide of manganese mixed with free sulphur, sulphuretted hydrogen being likewise evolved: hence these solutions contain sulphydrate of barium (BaHS) together with a polysulphide of barium. The third solution behaves like a solution of protosulphide of barium containing a slight excess of sulphuretted hydrogen. The fourth is of the same character, but contains a slight excess of baryta. This excess goes on continually increasing in the fifth, sixth and seventh solutions: and the eighth and ninth behave like pure baryta-water, yielding with chloride of manganese a white precipitate of manganous oxide. If the crude sulphide is at once treated with a quantity of water sufficient to dissolve the whole of the sulphide, the solution exhibits the characters of the pure protosulphide: it may however be a mixture of hydrate and sulphydrate of barium (see the above equation). A solution of sulphide of barium in not too large a quantity of water, kept for some years in a stoppered bottle, deposits, first crystals of hydrate of barium, then scales which are a mixture of crystallised hydrate of barium and the hydrated protosulphide ($Ba^2S.3H^2O$), and afterwards double six-sided pyramids containing the same substances, but much richer in sulphide of barium. The mother-liquor boiled down in a retort, evolves a continuous current of sulphuretted hydrogen, and on cooling deposits hydrated sulphide of barium in the form of a white powder, while sulphide of barium and hydrogen remains in solution.

Hydrated Sulphide of Barium, $Ba^2S.3H^2O$, is a white powder, which soon turns yellow. When treated at once with a quantity of water sufficient to dissolve it perfectly, it yields a solution which when mixed with a manganous salt, yields a precipitate of sulphide of manganese (Mn^2S) without evolution of sulphuretted hydrogen; but a smaller quantity of water extracts sulphydrate of barium and leaves hydrate of barium undissolved.

Sulphydrate of Barium, $BaHS$, or $BaS.HS$.—Baryta-water, or protosulphide of barium reduced to a paste with water, and warmed, is saturated with sulphydric acid, the solution evaporated apart from the air, and cooled, when crystals of baryta and yellow prisms are formed. The remaining liquid is either evaporated in a confined space, when white opaque prisms are obtained, or mixed with alcohol, filtered from the sulphur and hyposulphite of barium produced by air contained in the alcohol, and cooled down to —10° C.; in this way, colourless and transparent four-sided prisms are produced. Also when baryta or either of its hydrated compounds is allowed to crystallise, together with sulphide of barium, from an aqueous solution of protosulphide of barium, by evaporation in a retort and cooling, and the residual liquid (which is of a yellowish colour, from the air not being perfectly excluded) further evaporated and cooled, it solidifies to a crystalline mass of sulphydrate of barium (H. Rose). The crystals contain water, which they lose when heated, becoming white at the same time. When exposed to the air, they effloresce and turn white, while hyposulphite and sulphate of barium are formed. In a retort, they lose their water of crystallisation without fusing, and then evolve sulphydric acid as the temperature approaches redness, leaving dark yellow protosulphide of barium, which becomes white as it cools. An aqueous solution precipitates chloride of manganese, with escape of sulphydric acid gas (Berzelius, Pogg. Ann. vi. 441). The salt, when boiled, evolves sulphydric acid. With iodine, it forms iodide of barium and free hydriodic acid, sulphur being set free. It is insoluble in alcohol. (H. Rose.)

Trisulphide of Barium, Ba^2S^3, is said to be obtained, together with sulphate, by igniting 8 pts. of baryta with 6 pts. of sulphur, 1·78 pts. of the sulphur volatilising during the process. On treating the product with water, the trisulphide dissolves, and 2·8 pts. of sulphate of barium, remain behind (Vauquelin). When the moistened trisulphide is heated to redness and vapour of water is passed over it, sulphuretted hydrogen is given off, and sulphate of barium is formed. (Gay-Lussac.)

Pentasulphide of Barium, Ba^2S^5, is obtained in solution, by boiling the protosulphide or the sulphydrate with sulphur (H. Rose); also, together with hyposulphite of barium, by boiling baryta-water with sulphur. The solution is yellow, bitter, alkaline and caustic; leaves a pale yellow amorphous mass when evaporated in vacuo; and is decomposed by exposure to the air, with deposition of sulphur and formation of hyposulphite of barium.

BARLEY. See CEREALS.

BARNHARDTITE. A sulphide of copper and iron, $2Cu^4S.Fe^4S^3$, containing traces of silver, found in a mine in Barnhardt's Land, and other localities in North Carolina. Bronze-yellow, with metallic lustre, sometimes dull and opapue. Fracture conchoïdal; no cleavage. Specific gravity 4·521. Hardness = 3·5. Brittle. Streak greyish-black, somewhat shining. Tarnishes in the air, especially in contact with moisture, acquiring a brown or rose-red colour. Before the blowpipe, it gives the reactions of iron and copper. (Genth, J. pr. Chem. lxiv. 468.)

BAROCALCITE. Syn. with BARYTOCALCITE.

BAROLITE. Syn. with WITHERITE.

BAROMETER (*βαρος* weight and *μετρον* measure). The barometer is an instrument employed to measure the pressure or weight of the atmosphere. It consists essentially of a continuous body of liquid, generally mercury, from one part of the upper surface of which all pressure is removed, while the atmosphere still presses upon the remainder of the surface. It is a law of hydrostatics that, in a heavy fluid, the pressure at all points in a horizontal plane must be uniform, in order that there may be equilibrium. The surface of the mercury cannot, then, remain in one plane, as it does when the atmosphere presses equally on every part, but it must rise where protected from the atmosphere, until the pressure of the portion thus rising exactly balances and replaces the pressure of the atmosphere. Thus in *fig.* 92, the surface of mercury on which the atmosphere presses is at A, and the glass tube A B, having been perfectly emptied of air and every other fluid, the mercury has risen to B, so that the perpendicular column of mercury A B exerts a pressure at the horizontal plane A, exactly equal to the pressure of the atmosphere at A.

Now supposing mercury to be always of one specific gravity, the *length* of the barometric column will be exactly proportional to the *weight* or pressure of the atmosphere, and thus a length expressed in inches or parts of a metre becomes a convenient expression for a weight. It is well, however, to bear in mind the real pressures indicated, which are easily determined, as in the following example:—

29·872 inches = mean height of barometric column for noon at Greenwich.
13·568 = specific gravity of mercury at 60° F.
997·137 oz. avoirdupois = weight of one cubic foot of water at 62° F.

$$\frac{29\cdot872 \times 13\cdot568 \times 997\cdot137}{12 \times 12 \times 12} = 233\cdot879 \text{ oz.} = 14\cdot617 \text{ lbs.}$$

the average atmospheric pressure for noon at Greenwich on every square superficial inch.

Barometer at 28 inches	Atmospheric pressure 13·70 pounds
,, ,, 29 ,,	,, ,, 14·19 ,,
,, ,, 30 ,,	,, ,, 14·68 ,,
,, ,, 31 ,,	,, ,, 15·17 ,,

When any other liquid, is used, the height of the barometric column will be inversely as the specific gravity. Thus the height of a column of water corresponding to 29·872 inches of mercury at 60° F. is $29\cdot872 \times \frac{13\cdot568}{1\cdot000}$, or 405·3 inches or 33·77 feet; similarly a column of sulphuric acid would stand $29\cdot872 \times \frac{13\cdot568}{1\cdot85}$, or 219 inches high.

A full account of a water barometer constructed for the Royal Society by Professor Daniell will be found in Phil. Trans. cxxii. (1832), 539.

Construction of the Barometer.—All that is necessary to construct a barometer is to seal a glass tube about three feet along at one end, to fill it perfectly with mercury, and putting the finger over the open end, to invert the tube into a vessel of mercury. On withdrawing the finger, the mercurial column descends a few inches, and a measure being applied, the height of the column remaining is found. But to attain accuracy, great precautions are required at every step.

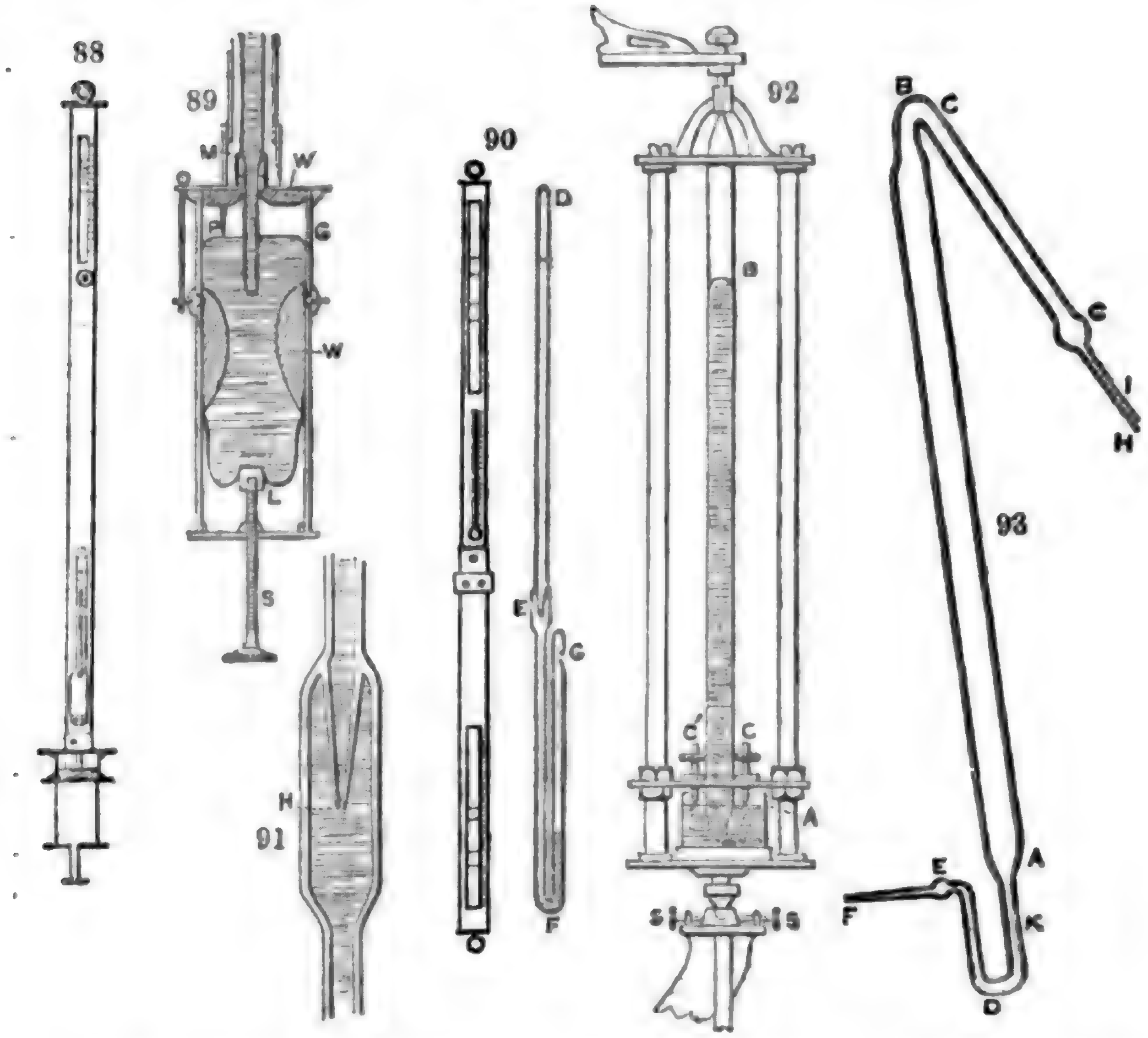
If any air remain in the tube, by adhering to the glass, it will rise into the space above the mercury, and its pressure, partly counteracting that of the atmosphere, will depress the barometric column. Most of the air may be got out by shaking the mercury in the tube, but some will certainly remain, to eliminate which, the tube must be boiled as follows:—Fill only about six inches of the tube with mercury, and gradually heat it over a strong flame or a charcoal fire until the mercury has boiled for a few moments. At the same time, heat another portion of mercury, that it may not crack the hot tube, and with it fill a few inches more of the tube. Expose this new part chiefly to the flame until it boils, and thus proceed, alternately pouring in a little mercury and then boiling, until the tube is almost full. It would be well to anneal the tube, if a large one, while cooling, to prevent fracture. When cold, fill it entirely with mercury, already boiled, and invert, with great precautions, to prevent entrance of air. Any kind of dirt entering also will prove very detrimental, and the tube, in the first place, before sealing, should be thoroughly sponged out with whiting and spirits of wine.

The mercury used must be perfectly pure, otherwise it will be thick, sluggish, and dirty, as well as somewhat false in specific gravity. To purify it, agitate with diluted nitric acid or sulphuric acid, and keep it under the acid, if possible, for a week or more, afterwards washing with fresh acid and distilled water. Carefully distilled mercury is pure enough, except that the dissolved oxide of mercury must be removed by treatment with sulphuretted hydrogen water, or dilute sulphide of ammonium.

Many forms of the barometer have been contrived since its first discovery by Torricelli; but, except in rendering the instrument portable and unalterable, no improvement has ever, or perhaps can ever be made on the original simple form. In fact, the most perfect barometer existing, the Great Standard at the Kew Observatory, mentioned further on, is also the most simple that could be imagined.

We shall, therefore, content ourselves with describing those forms of the barometer which can be recommended to the observer of the present day for their accuracy and convenience.

Figs. 88—93.



In *fig.* 88 is shown the PORTABLE STANDARD BAROMETER, as first invented by Fortin of Paris, and now made, amongst others, by Negretti and Zambra of Hatton Garden, London, at a cost of eight guineas.

The barometer tube has an internal diameter of ·39 or ·40 inch, and the air is perfectly driven out by the usual process of boiling. The cistern (*fig.* 89) is composed partly of a glass cylinder G, of boxwood sides and top, W and W′, and of a leather bag, L, the bottom of which can be raised or lowered by the finger-screw, S. The whole is, of course, held together by a brass casing, and the barometer tube, the lower end of which is contracted, is connected with the cistern by a leather joint at M.

To make an observation of this barometer, the lower surface of the mercury must first be adjusted so as just to touch the ivory fiducial point P (*fig.* 89), by turning the screw S. The moment of exact contact may be very accurately observed, if the mercury be properly clean and bright, by watching when the ivory point and its reflection just meet; if the mercury be even $\frac{1}{1000}$ of an inch too low, light will appear between the point and mercury; while, if too high, a small depression, instantly detected by reflected light, will be caused in the mercurial surface by the ivory point.

Next, the upper surface of the mercurial column is observed by adjusting the lower edge of a moveable brass cylinder, so that it shall visually be the tangent to, that is shall just touch, the curved surface of the mercury. To avoid the error of parallax, the line of vision must be exactly horizontal. The scale of inches, with the assistance of the vernier engraved on the moveable cylinder, then gives the actual height of the column, subject to index error, within the $\frac{2}{1000}$ part of an inch. But the observer, with a little practice, will soon discriminate the $\frac{1}{1000}$ part by the naked eye.

A Barometer should never be carried about in its ordinary upright position; for the mercurial column, being delicately balanced against the weight of the air, will be found to vibrate, or as it is said, to *pump* rapidly up and down when the barometer suffers any vertical disturbance. Not only might bubbles of air adhering to the lower part of the tube be thus carried up, but the mercury violently striking the sealed and vacuous end, might shatter a tube that was not very strong. To render this barometer portable, the handscrew at S must be screwed up, and the instrument gently inclined at the same time, until the mercury fills the whole of the tube, and *almost* the whole of the cistern; it is then to be inverted and kept or carried about as nearly as possible in this position until again safely suspended. A board and bracket, not shown in the figures, accompany this barometer, as also an arrangement of three screws, by which it may be secured motionless in the vertical position, which it of course assumes when free. Such a barometer is very suitable and quite good enough for a laboratory, or for a series of meteorological observations. It is the form of barometer most esteemed on the Continent.

Of **Mountain Barometers**, which require to be far more portable and secure from accident than that above described, the best is Gay-Lussac's form (see Ann. de Chimie, 1816, i. 113), as improved by Bunten, and drawn in *fig.* 90 from an instrument by Negretti and Zambra. Its tube is in the form of a syphon, of which the parts D E and F G have an uniform diameter of ·2 inch, while the part E F is a capillary tube, with a bore of about ·05 inch. The end of the tube at G is sealed, but a minute and somewhat sunken hole is pierced about an inch below the end, so that air may pass freely in or out, but not the mercury. At E is a pipette or air trap, shown on a larger scale in *fig.* 91, contrived by Bunten, so that even if air pass up the tube E F, it will collect at E, since it is scarcely possible that it should find its way through the capillary communication (H, *fig.* 91) into the upper part of the tube.

The tube is loosely packed in a brass tube-case, through two slits in which the upper and lower surface of the mercury may be observed in the same manner as the upper surface in the Fortin barometer. There are two divided scales, both 9 inches long, and measured from the lowest point of the lower scale, and the difference of the readings is the height of the barometric column. The verniers read to the $\frac{1}{1000}$ of an inch.

Newman's Standard Barometer is well known, and has long been relied upon in other countries as well as this. The tube has a diameter of ·5 or ·6 inch, and stands in a plain cylindrical glass cistern. The graduated scale is of brass, affixed to a brass rod passing down the inside of one of the upright supports, and terminating below in a conical ivory point, which by an endless screw and wheel is very accurately adjusted to contact with the mercury. In this respect the construction is superior to that of the Fortin barometer, because the mercury when raised or lowered, as in the latter, may not at once assume its true position, owing to adhesion. Mr. Newman has adopted a method of filling his barometer-tubes in vacuo, and of boiling them under diminished pressure, which obviates all oxidation and fouling of the tubes.

The Great Standard Barometer of the Kew Observatory, constructed by the late Mr. Welsh, has a tube 1·1 inch in bore, and as it was found impossible to fill so large a tube satisfactorily in the ordinary way, the following excellent method was adopted: — To the upper end of the barometer tube A B (*fig.* 93) was attached a capillary tube A D E F, much contracted at D, with a small bulb at E, drawn out at F to a fine point, and hermetically sealed. To the lower end of the large tube was attached 10 inches of a smaller tube B C G, having a bore of 0·3 inch, and to that again was added about 6 inches of capillary tube G H. A bulb of $\frac{3}{4}$ of an inch was blown at G, and the small tube finally bent into a syphon form at B. The end H of the capillary tube was now connected with a good air-pump, and the air very slowly extracted, at the same time that the whole tube was strongly heated by passing a large spirit flame along it. When the air had been as well as possible extracted, and whilst the pump was still in action and the heat still applied, the capillary tube G H was sealed at I by a blowpipe flame. When the tube had cooled, it was placed at a small inclination with the end F in perfectly pure mercury, which had been previously boiled, and the point being broken off, the mercury rose until the bulb at G was more than half filled. The point F was then again sealed, the capillary tube remaining quite filled with mercury. When the glass at F had cooled, the whole tube was inverted, the mercury now separating at the contracted part D, leaving the tube from D to F filled, or very nearly so, and from D to A perfectly vacuous. The operation was completed by sealing the tube at K, removing the portion K D E F, placing the bend B in the cistern of the barometer, and breaking off the tube C G at the point C.

The tube finally adopted at Kew, is perfectly free from air in the portion B, which is 9 inches long; it is mounted in an open brass frame (*fig.* 92), adjusted to verticality by screws at S; at C C′ are two steel rods, the first terminating below in a conical point, the second in a knife-edge, and both adjusted so as just to touch the surface of the mercury in the cistern. The height of the mercurial column is then easily observed by a cathetometer placed five feet off, the telescopic wire of which is made alternately to bisect a mark on the head of the rods C or C′, and to form a tangent to the mercurial surface at B. The difference of the readings on the divided scale of the cathetometer, added to the known length (3·515 for C) between the point and end of the steel rod, and the mark on its head, gives the actual length of the barometric column. The cistern of this barometer stands 33·9 feet above the mean sea-level. (Phil. Trans. [1856] p. 507.)

A very interesting account of the construction of the Royal Society's Standard barometer by Daniell, will be found in his Meteorological Essays, p. 353. See also Mr. Baily's Description of a New Barometer, Phil. Trans. cxxvii. 431; and Hudson, Phil. Trans. [1832] p. 575.

We will now consider the precautions and corrections necessary in obtaining the true atmospheric pressure with exactness.

Correction for Capacity.—It is obvious that in proportion as the barometer stands higher, so much more mercury there must be in the tube, and consequently so much less in the cistern. We should not then get the true variations in the length of the mercurial column, by noticing the top of the column only, since the base of the column also varies, and a correction must obviously be made for the amount of the variation.

This correction, indeed, is not required in any of the barometers above described, because observations or adjustments are made both at the upper and lower surfaces of mercury. But in many other barometers, the scale is measured truly from the lower surface of the mercury, only when the column is at one particular height, called the *neutral point*, usually determined by the barometer-maker, and marked on the instrument. When the column is higher or lower than this point, the mercury in the cistern must be lower or higher in a proportion depending on the sectional areas of the tube and cistern. If H be the height of the neutral point, and h the observed height of the barometer, the correction for capacity is

$$+\left\{\frac{\text{diameter of tube}}{\text{diameter of cistern}}\right\}^2(h-H)$$

In the marine barometer adopted by the Board of Trade, this correction is actually performed upon the divided scale, so that the inch divisions are about $\frac{1}{4}$ less than real inches. In any syphon barometer, like that of Gay-Lussac, in which both legs are of equal diameter, the correction for capacity is made by doubling the variations in height of one surface, and Gay-Lussac recommends this method when great nicety is not required; but measurements of both surfaces are evidently necessary for certainty.

Correction for Temperature.—The length of the barometric column is proportional to the pressure which it has to measure only so long as the specific gravity of mercury is constant. Now mercury expands $\frac{1}{10000}$ of its own volume when its temperature rises one degree (Fahr.), and its density of course varies inversely. Hence all readings of the barometer must be reduced to what they would be at one uniform temperature, that of 32° Fahr., when the specific gravity becomes 13·60. The brass scale by which the height is measured also expands by heat, and is only of the standard length when at a temperature of 62° F. (for the English yard).

To ascertain the temperature of the barometer, a thermometer is always attached. This should be placed half way up the barometer tube, with the bulb close to the tube, and well covered up from the atmosphere. The barometer should be placed in a room of which the temperature changes as little and as slowly as possible.

If h be the observed height of the barometer, and t its temperature in degrees Fahr., the height reduced to 32° F. is

$$h-h\times\frac{\cdot 0001001(t-32)-\cdot 000010434(t-62)}{1+\cdot 0001001(t-32)}$$

but it is quite exact enough to subtract (or *add* if t be less than 29° Fahr.) the following correction:

$$h\left\{(t-32)(\cdot 0001)-(t-62)(\cdot 00001)\right\}$$

The reader will observe that the *cubic*, not the linear, expansion of mercury is used in these formulæ, for it is on the cubic expansion that the specific gravity depends.

The correction is most conveniently obtained, however, from a table such as that on the following page, which applies to barometers with *brass scales*, extending from the cistern to the top of the mercurial column.

Table for the Temperature-correction of the Barometer.

Temp. °F.	28·5 inch.	29·0 inch.	29·5 inch.	30·0 inch.	30·5 inch.	Temp. °F.	28·5 inch.	29·0 inch.	29·5 inch.	30·0 inch.	30·5 inch.
31	·006	·007	·007	·007	·007	61	·083	·084	·086	·087	·089
32	·009	·009	·009	·009	·010	62	·085	·087	·088	·090	·091
33	·012	·012	·012	·012	·012	63	·088	·089	·091	·093	·094
34	·014	·014	·015	·015	·015	64	·090	·092	·094	·095	·097
35	·017	·017	·017	·018	·018	65	·093	·095	·096	·098	·100
36	·019	·020	·020	·020	·021	66	·096	·097	·099	·101	·102
37	·022	·022	·022	·023	·023	67	·098	·100	·102	·103	·105
38	·024	·025	·025	·026	·026	68	·101	·102	·104	·106	·108
39	·027	·027	·028	·028	·029	69	·103	·105	·107	·109	·110
40	·029	·030	·030	·031	·031	70	·106	·108	·109	·111	·113
41	·032	·033	·033	·034	·034	71	·108	·110	·112	·114	·116
42	·034	·035	·036	·036	·037	72	·111	·113	·115	·117	·119
43	·037	·038	·038	·039	·040	73	·113	·115	·117	·119	·121
44	·040	·040	·041	042	·042	74	·116	·118	·120	·122	.124
45	·042	·043	·044	·044	·045	75	·118	·120	·122	·125	·127
46	·045	·045	·046	·047	·048	76	·121	·123	·125	·127	·129
47	·047	·048	·049	·050	·051	77	·123	·126	·128	·130	·132
48	·050	·051	·052	·052	·053	78	·126	·128	·130	·133	·135
49	·052	·053	·054	·055	·056	79	·128	·131	·133	·135	·137
50	·055	·056	·057	·058	·059	80	·131	·133	·136	·138	·140
51	·057	·058	·059	·060	·061	81	·134	·136	·138	·141	·143
52	·060	·061	·062	·063	·064	82	·136	·138	·141	·143	·146
53	·063	·064	·065	·066	·067	83	·139	·141	·143	·146	·148
54	·065	·066	·067	·068	·070	84	·141	·144	·146	·149	·151
55	·068	·069	·070	·071	·072	85	·144	·146	·149	·151	·154
56	·070	·071	·073	·074	·075	86	·146	·149	·151	·154	·156
57	·073	·074	·075	·076	·078	87	·149	·151	·154	·157	·159
58	·075	·077	·078	·079	·081	88	·151	·154	·157	·159	·162
59	·078	·079	·080	·082	·083	89	·154	·156	·159	·162	·165
60	·080	·082	·083	·085	·086	90	·156	·159	·162	·164	·167

The full tables, as originally calculated by Prof. Schumacher (Jahrbuch für 1837, Astron. Nach. t. ii.), will be found in the "Report of the Committee of the Royal Society on Physics," 1840. The Admiralty "Manual of Scientific Enquiry," and most works on Physics and Meteorology, also contain tables, often slightly differing from each other.

To obtain an approximate correction, multiply the number of inches in the height of the reading by the number of degrees Fahr. above 32°, and subtract ·0001 inch for every unit of the result. The following data are useful.

	For 1° Fahr.	For 1° Centigrade.
Coefficient of the cubic expansion of mercury (log. 1·0001001 = 0·0000435)	·0001001	·00018018
Coefficient of the linear expansion of brass	·00000956	·00001722
Coefficient of the linear expansion of brass adopted by Schumacher	·0000105	·0000188
Coefficient of the linear expansion of glass.	·0000048	·0000086

The last must be employed instead of the coefficient of brass, when the scale is engraved on the glass barometer tube, as often occurs on the Continent. Tables for glass metre scales and centigrade degrees, will be found in Bunsen's Gasometry, translated by Roscoe.

The Capillary Depression of the mercurial column is a formidable obstacle to the attainment of accuracy when the tube is of small bore. For this reason, important standard barometers, like that of Kew, have a large tube in which the capillary depression is inappreciable.

The cause of the depression is, that the particles of the mercury have a much stronger attraction for each other than for the glass; a slight resultant attraction thus arises, tending to draw each particle towards the general mass of mercury. The form which the surface of the mercury assumes is spheroïdal; the highest point of the surface is to be always taken, in adjusting the edge of the vernier for an observation.

To avoid any error from the capillary depression, it is far the best way to compare the barometer with an undoubted standard barometer in which the capillary depression is inappreciable. The correction for capillarity is then merged into that for index error.

If this be not done, the *bore* of the barometer tube must be ascertained from the barometer maker, or otherwise, and the correction then taken from the following table, which is the one generally adopted for the purpose in England.

Diameter of tube.	Add to the reading for		Diameter of tube.	Add to the reading for	
	Unboiled tubes.	Boiled tubes.		Unboiled tubes.	Boiled tubes.
0·60 inch.	0·004 inch.	0.002 inch.	0·30 inch.	0·028 inch.	0·014 inch.
0·50 „	0·007 „	0·003 „	0·25 „	0·040 „	0·020 „
0·45 „	0·010 „	0·005 „	0·20 „	0·060 „	0·029 „
0·40 „	0·014 „	0·007 „	0·15 „	0·088 „	0·044 „
0·35 „	0·020 „	0·010 „	0·10 „	0·142 „	0·070 „

Continental observers have attempted to attain greater accuracy by making the height of the meniscus or curved surface of the mercury an *argument* in the correction. M. Delcros has calculated an elaborate table on this principle of which a part is here given.

Bore of the tube. Millimetres.	Height of the meniscus in millimetres.								
	0·2	0·4	0·6	0·8	1·0	1·2	1·4	1·6	1·8
3·0	0·24	0·48	0·70	0·90	1·07	1·20	1·32		
4·0	0·12	0·24	0·35	0·46	0·55	0·63	0·71	0·77	
5·0	0·07	0·13	0·19	0·25	0·30	0·35	0·40	0·44	
6·0	0·02	0·06	0·09	0·13	0·18	0·20	0·23	0·25	0·27
7·0	0·01	0·03	0·06	0·09	0·10	0·12	0·14	0·15	0·16

For the full tables and for a very elaborate description of the principal standard barometers on the continent, the determination of their mean differences, and the errors to which barometers are subject, the reader should consult a paper by Bravais and Martius in Nouv. Mém. de l'Acad. Roy. de Bruxelles xiv. 31 (1841); see also Dove, Repertorium der Physik, i. 37.

The capillary depression of the barometric column has been investigated mathematically by Mr. Ivory in the Philosophical Magazine and Annals for 1828, vol. iii. p. 1. [This reference is usually wrongly given to the Philosophical Transactions.]

This correction is considered unnecessary to the Gay-Lussac, or any other syphon barometer, in which the two surfaces of mercury are of equal extent, and therefore subject to equal capillary action. But we think that the adhesion of the mercury in the lower limb of the Gay-Lussac tube, being much increased by the presence of air and dust, is liable to cause inaccuracy unless carefully attended to.

The Index Error is properly the error in the length of brass rod or scale extending between the two surfaces of mercury. Such error may usually be considered uniform for all parts of the divided scale, which is accurately divided by a machine, and the error probably arises, if at all, from the wrong adjustment of the ivory fiducial point.

But the index error, as usually determined by comparison with a standard barometer, comprises the capillary depression before mentioned, as well as any minute errors from impurity in the mercury, from imperfect vacuum in the upper part of the tube, error of the attached thermometer, and so on. Comparison with a standard, in short, secures the final accuracy of the result, and no observer of the present day who desires to be considered trustworthy should use an uncompared barometer. The purchaser of a barometer for scientific purposes should insist on receiving with it an authentic certificate of its index error from comparison with the Greenwich, Kew, or Royal Society Standard. The best barometer makers, Negretti and Zambra, Newman of Regent Street, or Barrow of Oxenden Street, the latter the maker to the British Meteorological Society, will readily procure such a certificate. Of course a fresh comparison is necessary if the barometer be in any way disordered or suspected of being disordered.

To compare two barometers, they should be suspended side by side, and a score of simultaneous readings of each taken at intervals, if possible when the barometric column is at various heights, and both rising and falling. The readings of each barometer are to be fully and carefully corrected for temperature, according to its own attached thermometer; the mean difference of all the readings, together with the known index error of the one barometer, is the index error of the other barometer.

From the uniformity of the readings, the observer may judge either of his own skill or of the character of the instruments. With good instruments and a careful observer, the differences should be uniform within about $\frac{2}{100}$ of an inch, and the whole index error, apart from capillary action, should not exceed $\frac{2}{100}$ or $\frac{3}{100}$; thus, in the comparison of the writer's barometer by Mr. Glaisher at Greenwich, the differences of twenty readings vary from $-0{\cdot}009$ to $-0{\cdot}020$, with a mean error of $-0{\cdot}014$, apart from the assumed capillary depression ·008 inch, making the whole correction $+{\cdot}022$ inch.

Treated according to the formulæ of the calculus of probabilities, the *probable error* of this determination from the mean of twenty observations is rather less than ·0015 inch. Assuming the Greenwich standard to be absolutely correct, this probable error of ·0015 inch is the only source of error which would not be eliminated by a proper use of the instrument, and in the taking of a number of observations, as is always the case in meteorology.

It is curious that a barometer maker, named Assier-Perricat, of Paris, as long ago as 1802, practised and advocated the method of ensuring the accuracy of barometers by comparison. (Assier-Perricat, Nouveau Traité sur l'Invention des Barometres, etc.)

It is important to be able easily to detect the presence of any air which might by accident get into the upper part of the barometer tube, where it would falsify the reading by a minute direct pressure, and probably also by increasing the capillary action. There happens to be a ready and perfect test as follows:—Incline the barometer so that the mercury may run up and strike the sealed end of the tube; if the sound be sharp and metallic, repeat the experiment several times, each time more gently. If the least trace of air be present, the sound will at last become soft and puffy; if, on the contrary, the vacuum be perfect, the sound will always remain beautifully clear and distinctly metallic.

If air be thus detected, uncover and examine the end of the tube, to see how large a bubble remains when the barometer is laid flat. Also invert the instrument and tap it, as sharply as is safe, near the bubble, which may sometimes be thus dislodged and eliminated. We do not think that a minute quantity of air can sensibly affect the reading of the barometer for ordinary purposes, but if there be more, the instrument must certainly be disused until refilled by the maker. If important observations have been made with a barometer containing air, they may be corrected, if the barometer be compared with a true one before its condition is altered. The simple difference of readings will be an approximate correction, but the exact correction is

$$\frac{e_1 e_3(h_2 - h_1)}{e_1(h - h_1) + e_2(h_2 - h)}$$

in which e_2 and e_3 are the errors of the readings h_1 and h_2 at different points of the scale, as determined by comparison, and h is the reading to be corrected.

If we suppose a bubble of air of $\frac{1}{50}$ of an inch diameter at the atmospheric pressure to enter the vacuous space of the Fortin barometer, described above, the depressing effect on the mercurial column may, by a simple calculation, be shown not to exceed $\frac{3}{10000}$ of an inch, apart, however, from any influence on the capillarity, a point probably of much greater importance than the direct effect.

DIRECTIONS FOR TAKING AN OBSERVATION OF THE BAROMETER.

1. Read and record the attached thermometer, making a correction for index error if necessary (see THERMOMETER).
2. Adjust the mercury below to exact contact with the fiducial point.
3. Slightly tap the tube near the upper end of the column, and adjust the edge of the vernier to exact tangential contact, the line of vision being horizontal.
4. Record the reading and work out the correct height as soon as convenient afterwards, as shown in the following example, which comprises all the corrections ever required:—

			Inches.
Attached thermometer . .	58·3 F.	Barometer reading . .	29·964
Data. Neutral point . .	28·861	Correction for capacity .	+·033
Capacity . . .	$\frac{1}{33}$	,, ,, capillarity	+·007
Diameter of the tube .	·4 inch		30·004
Index error to K. O. Standard (apart from capillarity) .	−·014 inch	,, ,, temperature	−·080
		,, ,, index error	−·014
		True height of the barometer	29·910

When many observations of one barometer have to be made, much labour will be saved by combining all these corrections into a special table, one reference to which furnishes the required correction. In important observations or comparisons, the adjustments and vernier readings should be made with a pocket lens.

It is much to be desired that the English should adopt the metre scale for the barometer, which is used all over the Continent; but although this may at once be done in chemical matters, it seems almost impossible at present in meteorology. For the easy reduction of the barometer scale from millimetres into English inches and *vice versâ*, we give the following tables. Negretti's portable barometer may be had with both millimetre and inch scales attached.

Millimetres	Inches.	Millimetres.	Inches.	Millimetres.	Inches.
700	27·560	751	29·567	762	30·000
705	27·756	752	29·607	763	30·040
710	27·953	753	29·646	764	30·079
715	28·150	754	29·685	765	30·119
720	28·347	755	29·725	766	30·158
725	28·544	756	29·764	767	30·197
730	28·741	757	29·804	768	30·237
735	28·938	758	29·843	769	30·276
740	29·134	759	29·882	770	30·315
745	29·331	760	29·922	771	30·355
750	29·528	761	29·961	772	30·384

1 millimetre = 0·03937 inch
0·1 „ = 0·00394 „
0·01 „ = 0·00039 „

1 inch = 25·39954 millimetres
0·1 „ = 2·53995 „
0·01 „ = 0·25400 „
0·001 „ = 0·02540 „

Uses of the Barometer.—The chemist requires to know the atmospheric pressure when very accurate weighings are made of light bodies, in order that the weight of the air they displace may be allowed for. On this subject, see Bessel's formulæ in the article Specific Gravity. Secondly, gases are usually weighed or measured, subject to the atmospheric pressure, and vary *directly in density* and *inversely in volume* with the pressure. Hence the atmospheric pressure must always be observed at the moment, in order that the weight or measure may be reduced, by a simple calculation, to what it would be at some standard pressure, which in England is 30·000 inches, and on the Continent 760 millimetres or 29·922 inches. Now $\frac{30{\cdot}000}{29{\cdot}922} \times 100 = 100{\cdot}261$ or 100 cubic inches of gas at the English standard pressure are equal to 100·261 cubic inches at the French standard pressure. It happens, however, that the English adopt 60° F. and the French 32° F., as the standard temperatures in these matters, and allowing for the expansion of mercury between these points, 29·922 inches become 30·006. Hence the true equivalent volume on the continental standard for 100 cubic inches of gas at 30·000 inch, 60° F., is $\frac{30{\cdot}000}{30{\cdot}006} \times 100 = 99{\cdot}98$ cubic inches, the difference being so trifling that it may almost always be neglected.

Determination of Altitudes.—Since the barometer measures the weight of the *superincumbent* air, the higher we rise in the atmosphere the lower the barometer must stand. At the surface of the earth, the barometer changes nearly ·001 inch for every foot in the change of altitude; but more exactly, the change of elevation corresponding to ·001 inch of the barometer, is:—

At temperature of 30°	0·865 foot
„ „ „ 40°	0·883 „
„ „ „ 50°	0·900 „
„ „ „ 60°	0·918 „
„ „ „ 70°	0·936 „
„ „ „ 80°	0·954 „

The difference of level (= x feet) of two barometers may be calculated by the following formula:

$$x = 60345{\cdot}7 \times \left\{ 1 + 0{\cdot}002837 \cos 2 \text{ lat.} \right\} \times \left\{ 1 + \frac{T + t}{900} \right\} \log \frac{B}{b}$$

in which B and b are the simultaneous corrected heights of the barometers at the higher and lower stations, and T, t the numbers of degrees Fahr. above 32°, at which the thermometers stand. (Biot, Traité de Physique, i. 100.)

If the height does not much exceed 3000 feet, the following more simple formula may be used:

$$x = 52494{\cdot}3 \times \frac{B - b}{B + b} \times \left\{ 1 + \frac{T + t}{900} \right\}$$

In meteorological observations, it is necessary to know the height of the barometer above the mean sea level, and to reduce the average results to that level accordingly, in order that they may be comparable with observations made at other places, and reduced in a similar manner.

Meteorology.—The chief use of the barometer is of course in meteorology, since changes of pressure in the atmosphere are the immediate cause of all winds. These changes are extremely complicated and interesting: for besides the irregular fluctuations, and extraordinary disturbances during storms, there is an average change, according to the season, and a semidiurnal oscillation, probably due to a kind of atmospheric tide, caused by the expansion of the atmosphere, where it is heated by the sun's rays (Phil. Mag. [4] xvii. 313). In keeping a register of the barometer, it should be observed every day at 9 A.M., the time of the daily maximum, and at 3 P.M., the time of daily minimum, or else at noon, when the pressure is near the mean.

The nightly maximum is about 9 P.M., the nightly mininum about 4 A.M. Almost every climate, however, is characterised by special laws of barometric fluctuation.

Aneroid Barometer. (α, priv. νηρος, liquid).—The essential part of this beautiful instrument is a small round metal box, exhausted of air, and with a thin circularly fluted lid, which the weight of the atmosphere more or less tends to press in. A complicated system of levers, causes an index, revolving over a dial, to mark the slightest movements of this metal lid. (Vidi, Compt. rend. xxiv. 275; Belville's Manual of the Mercurial and Aneroid Barometers.)

Bourdon's Metallic Barometer also consists of a vacuous metal box, but it is in the form of a flat tube bent almost into a circle. The two ends of the tube approach or recede as the atmospheric pressure increases or diminishes.

These metallic barometers are very sensitive and excellent as weather glasses, and they should be carried at sea or on exploring expeditions as a last resource in case the mercurial barometers, as often happens, become disordered. But they afford no independent measure of pressure, and are so much affected by variations of temperature as to be unsuitable for scientific use. The writer, however, has used an aneroid barometer with some success, and obtained an approximate correction for temperature by simply warming the instrument on various occasions, and noting the average change of reading (= ·0065 inch per degree F.) thus caused. An adjusting screw will be found at the back of the aneroid barometer, by which its reading may be made to agree at some one point and temperature with that of a mercurial barometer.

For a description of Macworth's "Underground barometer," see *Ure's Dictionary of Arts, Manufactures, and Mines*, i. 255.) W. S. J.

BARRAS. The resinous incrustation in the wounds made in fir-trees.

BARSOWITE. A silicate of calcium and aluminium found near the river Barsowka in the Ural, in compact white masses or fine-grained aggregations, having a distinct cleavage in one direction. The granular variety has a faint mother-of-pearl lustre: the compact variety is dull and translucent on the edges. Sp. gr. 2·740 to 2·752. Hardness 5·5 to 6·0. Before the blowpipe, it melts with difficulty to a tumefied glass on the edges: with borax, slowly and quietly to a transparent colourless glass; likewise with phosphorus-salt, with separation of silica, the glass becoming opalescent on cooling if the proportion of the mineral is considerable. With an equal weight of carbonate of sodium, it melts to a tumefied glass, which with a larger quantity of soda, becomes snow-white and infusible. With solution of cobalt, it becomes blue on ignition. The powder is easily decomposed by hydrochloric acid, forming a thick jelly. According to Varrentrapp's analysis, it contains $3(2Ca^2O.SiO^2).(4Al^4O^3.3SiO^2)$ a small quantitiy of the lime being replaced by magnesia. (Handw. d. Chem. 2te Aufl. ii. 679.)

BARWOOD or **CAMWOOD.** A red dye-wood, the colouring matter of which appears to be identical with santolin (Preisser und Girardin, Ann. Ch. Pharm. lii. 375.) See also *Ure's Dictionary of Arts, Manufactures and Mines*, i. 255.)

BARYTA. See Barium, Oxides of.

BARYTES, BARYTINE, or **BAROSELENITE.** See Heavy Spar.

BARYTIC FLUORSPAR. A mixture of about equal parts of sulphate of barium and fluorspar, occurring on the slaty limestone of Derbyshire, where it forms a bed about an inch thick.

BARYTO-CALCITE, $BaCaCO^3$ or $BaO.CO^2 + CaO.CO^2$; a mineral found in Cumberland, of a slightly yellowish-brown tinge, translucent, with a waxy lustre, and sp. gr. 3·66. It contains cavities which are lined with crystals having the form of oblique rhombic prisms. The external surface is coated with sulphate of barium. (Brooke, Ann. Phil. N.S. viii. 114.)

The name baryto-calcite was also given by Thomson to a laminated mineral containing 71·9 p. c. sulphate of barium and 28·1 sulphate of calcium, found between Leeds and Harrogate in Yorkshire; also by Johnston to Alstonite, which is of the same composition but different crystalline form.

BARYTO-CŒLESTIN. This name is given to two minerals, both consisting of sulphate of barium and sulphate of strontium (cœlestin), one occurring near Kingstown in Canada, the other in the Binnenthal in Switzerland. The Swiss mineral forms orthorhombic crystals, containing, according to Waltershausen (Pogg. Ann. xciv. 134), 87·8 p.c. sulphate of barium and 9·1 sulphate of strontium. The Canadian mineral occurs in crystalline masses, containing, according to Thomson, $Ba^2Sr^4.3SO^4$. Allied to this is a mineral from the chalk marl of Moen, containing 40 p.c. Sr^2SO^4, 28·3 Ba^2SO^4, 15·5 Ca^2SO^4, 13·5 Ca^2CO^3, and 2·5 water.

BARYTOPHYLLITE. Syn. with CHLORITOÏDE.

BASALT. A rock of volcanic origin, occurring in amorphous masses, columnar, amygdaloïdal, and vesicular. Its colours are greyish-black, ash-grey, and raven-black. Massive, with dull lustre and granular structure. Fracture uneven or conchoïdal. Concretions columnar, globular, or tabular. It is opaque, yields to the knife, but is not easily frangible. Streak light ash-grey. Sp. gr. 3. Melts into a black glass and recovers its granular structure by slow cooling. It is found in beds and veins in granite and mica slate, the old red sandstone, and coal formations. It is distributed over the whole world, and is met with in great variety in Scotland.

The most remarkable variety of basalt is the columnar, which forms immense masses, composed of columns thirty, forty, or more feet in height, and of enormous thickness; those at Fairhead are two hundred and fifty feet high. These constitute some of the most astonishing scenes in nature, for the immensity and regularity of their parts. The coast of Antrim in Ireland, for the space of three miles in length, exhibits a very magnificent variety of columnar cliffs; and the Giant's Causeway consists of a point of that coast formed of similar columns, and projecting into the sea upon a descent for several hundred feet. These columns are, for the most part, hexagonal, and fit very accurately together; but most frequently do not adhere together, though water cannot penetrate between them. Another very remarkable formation of columnar basalt is the island of Staffa on the west coast of Scotland. The most extensive mass of basalt yet observed is that discovered by Colonel Sykes in the Deccan, where it occupies a surface of many thousand square miles.

Basalt is not a mineral of definite constitution, but a mixture of several minerals, generally of labradorite, augite, olivine, magnetic iron ore, and a zeolite. These minerals may however be replaced by others, namely labradorite by other varieties of felspar, and augite by amphibole: the zeolitic portion also varies greatly in composition. Some of the constituents of basalt viz. the olivine, the magnetic iron ore and the zeolite are decomposible by hydrochloric or sulphuric acid; the rest for the most part resist the action of acids; but the analytical results obtained by this mode of treatment are not very definite, inasmuch as the action of the acid varies with its strength, with the state of aggregation of the basalt, and with the nature of the individual minerals of which it is composed. The constituents of basalt, are silica (about 50 per cent.) alumina, protoxide of iron, lime, magnesia, potash, soda and water, the proportions of which differ considerably in the several varieties of basalt, as shown by the numerous analyses which have been made of it.

Basalt when calcined and pulverised, is said to be a good substitute for pozzolana in the composition of mortar, giving it the property of hardening under water. Wine bottles have likewise been manufactured with it, but there appears to be some nicety required in the management to ensure success. A mixture of 1 pt. basalt, 2 pts. broken glass, 2 soda, 1 wood-ash, and $\frac{1}{50}$ peroxide of manganese, has also been used for similar purposes.

BASALTIC HORNBLENDE usually occurs in opaque six-sided crystals, which sometimes act on the magnetic needle. It is imbedded in basalt or grauwacke. Colour velvet-black. Lustre vitreous. Scratches glass. Melts with difficulty to a black glass. Contains 47 per cent. silica, 26 alumina, 8 lime, 2 magnesia, 15 iron, and 0·5 water. It is found in the basalt of Arthur's Seat, in that of Fifeshire, and in the Isles of Mull, Canna, Eigg, and Skye; also in the basaltic and floetz traps of England, Ireland, Saxony, Bohemia, Silesia, Bavaria, Hungary, Spain, Italy, and France. U.

BASANITE. See JASPER.—**BASANOMELANE.** See ILMENITE.

BASE. This term is the correlative of ACID, and denotes the electropositive constituent of a salt. Its signification varies, however, to a certain extent, according to the view which is taken of the constitution of salts. In the dualistic system, which regards salts as formed by the union of two binary compounds of the first order, *e.g.* sulphate of copper = $Cu^2O.SO^3$; sulpharsenate of potassium = $3K^2S.As^2S^5$: hydrochlorate of ammonia = $NH^3.HCl$; nitrate of ethylamine = $NH^2(C^2H^5).HNO^3$, &c.; the base is the electropositive oxide, sulphide, selenide, or alkaloïd, which unites with the electronegative oxide, sulphide, &c., or hydracid; but in the unitary system, in which the salts of any acid are regarded as formed on the same type as the acid (or hydrogen-salt) itself, the base must be understood as the metal or other electropositive radicle by which the hydrogen of the acid is replaced: thus in the salts above-mentioned, regarded as Cu^2SO^4, K^3AsS^4, NH^4Cl, $NH^3(C^2H^5).NO^3$, the bases are the radicles Cu, K, NH^4, $NH^3(C^2H^5)$. (See ALKALIS, ALKALOIDS, AMINES, AMMONIUM-BASES, OXIDES, RADICLES.)

BASICERINE. See HYDROCERITE.

BASICITY. The power of an acid to unite with one or more atoms of base. See ACIDS, p. 46.

BASILICUM, OIL OF. The leaves of the *Ocymum basilicum*, a plant belonging to the labiate order, yield by distillation with water, an essential oil, which after a while deposits prismatic crystals, having the character and composition of hydrate of turpentine, $C^{10}H^{22}O^3 = C^{10}H^{16}.3H^2O$ (Dumas and Péligot). The oil itself has not been examined.

BASSIA LATIFOLIA. The seeds of this plant, which grows on the Himalayas, yield by pressure a yellowish oil, which gradually becomes colourless on exposure to light, has a faint odour, a density of 0·958, and a buttery consistence at ordinary temperatures; melts at 27° to 30° C.; dissolves sparingly in anhydrous alcohol, scarcely at all in spirit of ordinary strength, readily in ether. By saponification it yields, besides oleic acid and glycerin, two fatty acids, one which has not been obtained pure, but appears to have the composition $C^{15}H^{30}O^2$; the other, originally supposed to be a peculiar acid, and called *bassic acid*, is identical in composition and properties with stearic acid, $C^{18}H^{36}O^2$. (Hardwicke, Chem. Soc. Qu. J. ii. 231.)

BASSORIN. The principal constituent of *Gummi bassoræ*, *G. Toritonense*, or *G. Kutera*, a gum obtained from various species of acacia. This gum contains only about 5·6 per cent. of matter soluble in water (arabin), while the larger proportion, which is the bassorin, merely swells up in water. (See GUM.)

BASTARD CLOVER. *Trifolium hybridum.*—100 pts. of the fresh flowering plant yield 2·44 pts. of ash; 100 pts. of the dry plant 8·1 pts. of ash. The ash contains in 100 pts. 19·9 potash, 5·7 soda, 18·4 lime, 3·1 magnesia, 5·6 alumina (?), 3·9 sesquioxide of iron, 1·8 protoxide of manganese (?), 35·1 silica, 1·4 sulphuric anhydride, 4·5 phosphoric anhydride, 0·6 chlorine. (Sprengel, J. pr. Chem. x. 56.)

BASTITE. A mineral found at Basti in the Harz, and forming imperfectly defined individual crystals intergrown with serpentine. It cleaves very easily in one direction, less easily in another, making an angle of 87° with the first; there are also two imperfect cleavage-planes in the direction of the longitudinal and lateral faces. Fracture, uneven and splintery. Colour, leek to olive green, passing into yellow and brown. It has a metallic, glittering, nacreous lustre on the cleavage-faces; translucent on the edges. Specific gravity 2·6 to 2·8. Hardness 3·5 to 4·0. Gives off water when heated, and before the blowpipe becomes pinchbeck-brown and magnetic; it then splinters, melting to a brown glass on the edges. With borax and phosphorus-salt, it gives the reactions of iron and chromium, and with the latter a skeleton of silica. It is imperfectly decomposed by hydrochloric, completely by sulphuric acid. Its composition is nearly represented by the formula $4Mg^2H^4O^3 . 3(Mg^4 \text{ or } Fe^4)Si^3O^8$ which, if the hydrogen be regarded as basic, may be reduced to the general form $M^{36}Si^9O^{36}$, that is to say to the formula of an orthosilicate M^4SiO^4. Hermann regards the mineral as crystallised serpentine somewhat altered in composition by admixture of foreign minerals; but its form indicates rather a relation to the augite family. (Handw. d. Chem. i. 756.)

BASYL. Graham's name for the metal or other electropositive constituent of a salt (Elements of Chemistry, 2nd ed. i. 186).

BATATAS EDULIS. Sometimes called *Convolvulus batatas* or *Spanish potato*, a plant said to be indigenous in India, but extensively cultivated in America, and sometimes also in the south of Europe. The tubers resemble those of the potato, but have a sweeter taste. According to T. J. Herapath (Chem. Soc. Qu. J. iii. 194), they contain, in the fresh state, 66·7 per cent. water and other volatile matter, 31·8 vegetable matter, and 1·5 inorganic matter. The ash contains in 100 pts.: —

(*a.*) *Soluble in water.* — 8·7 CO^2, 7·1 SO^3, 0·9 P^2O^5, 29·3 K^2O, 12·4 KCl, and 11·4 NaCl.

(*b.*) *Insoluble.* — 6·2 CO^2, 7·1 P^2O^5, 12·0 Ca^2O, 1·4 Mg^2O, 1·3 Fe^4O^3, 2·1 SiO^2, with traces of sulphuric acid and alumina.

According to Henry (J. Pharm. xi. 223) the tubers contain in 100 pts. 13·3 starch, 0·9 albumin, 3·3 sugar, 1·1 fat insoluble in ether, 6·8 woody fibre, 1·4 malic acid, acid phosphates, chloride of potassium, &c., and 73·1 water, also 0·05 of a volatile poisonous matter.

BATH. The heat communicated from lamps and fires is subject to variation from many circumstances; and this variation not only influences the results of operations, but often endangers the vessels, especially if they are made of glass. To obviate these sudden changes of temperature, and at the same time to afford means of observing and regulating the degree of heat imparted, the vessel containing the substance operated upon is immersed in another containing water, oil, fusible metal, air, or other medium, which receives the heat directly from the source. The sand-bath and water-bath are most commonly used, the latter for maintaining a substance for any length of time at the constant temperature of 100° C., the former for higher temperatures, particularly when the exact observation of the temperature is not an object. In using the water-bath, the vessel to be heated may, according to convenience, be either immersed in the water or so placed above the vessel that its lower surface may be in contact with the steam. A ready method of constructing a water-bath for small operations is to place the basin containing the substance to be heated on the top of another of equal size, containing water and supported over a gas lamp.

The temperature of the water-bath may be raised above 100° C., by dissolving certain salts in the water. A saturated solution of common salt boils at a temperature of 7°·5 C. or 13°·3 F., above the boiling point of water; and by using a solution of chloride of calcium, a bath of any temperature between 100° and 125° C. or 212° and 252° F. may be conveniently obtained.

Liquid baths of higher temperature are obtained by the use of linseed oil or fusible metal heated in cast-iron pots. The oil-bath may be used for temperatures up to about 300° C., but it is dirty, and exhales an extremely unpleasant odour when strongly heated. Fusible metal is much cleaner and more pleasant to use, but its weight is an inconvenience where a large bath is required. A thermometer immersed in the liquid, as near the middle as possible, serves to indicate the temperature. The oil-bath is much used in the determination of vapour-densities by Dumas's method, also for heating volatile substances or mixtures in sealed tubes, so as to subject them to a higher tem-

Fig. 94.

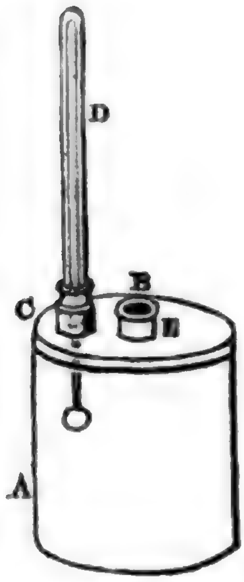
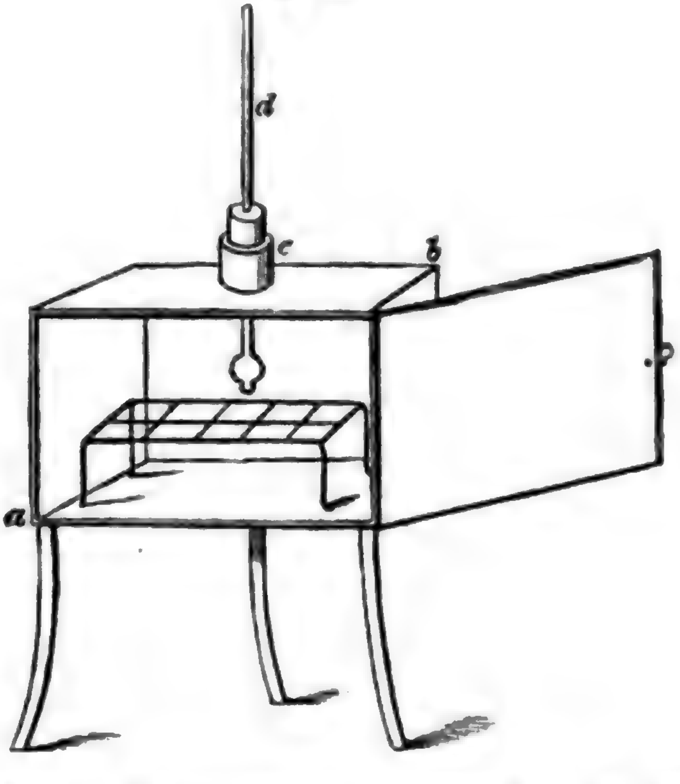


Fig. 95.



perature than that to which they could be exposed under the ordinary atmospheric pressure. The danger of explosion attending this operation may be obviated by enclosing the sealed glass tube in a strong tube of wrought iron, having a massive screw cap.

The air-bath is very convenient for many purposes, especially for desiccation. An air-bath may be extemporaneously constructed by placing an empty basin over a lamp, and another basin containing the substance to be dried on the top of it. The upper vessel is then heated by the air in the intervening space. A more convenient apparatus, which also serves to indicate the temperature, consists of a cylindrical copper vessel A, *fig.* 94, the cover of which is movable and has two apertures, the middle serving for the escape of vapour and the lateral one for the insertion of the thermometer. The vessel to be heated rests on a ring within the box, supported by a tripod. A larger air-bath serving to heat several small vessels at once is represented in *fig.* 95. Air-baths are sometimes surrounded with a jacket to hold water or oil. When water is used, the temperature of course cannot exceed 100° C. When oil is used, the temperature is indicated by a thermometer having its bulb immersed in the liquid.

High-pressure baths.—The danger of explosion in heating volatile liquids in sealed tubes is greatly diminished, when the tubes are at the same time subjected to a pressure from without. This may be effected by enclosing the tube containing the volatile liquid in a wider glass tube containing a less volatile liquid, and likewise sealed; the whole is then heated in an oil- or air-bath. In this manner, alcohol or ether may be heated to 360° C., the outer tube containing oil of turpentine (**Berthelot**). Greater security is obtained by enclosing the glass tube in a wrought iron tube, with a screw-cap, or by the use of a Papin's digester, or better, by the following apparatus invented by **Frankland** (Ann. Ch. Pharm. xcv. 30).

Fig. 96.

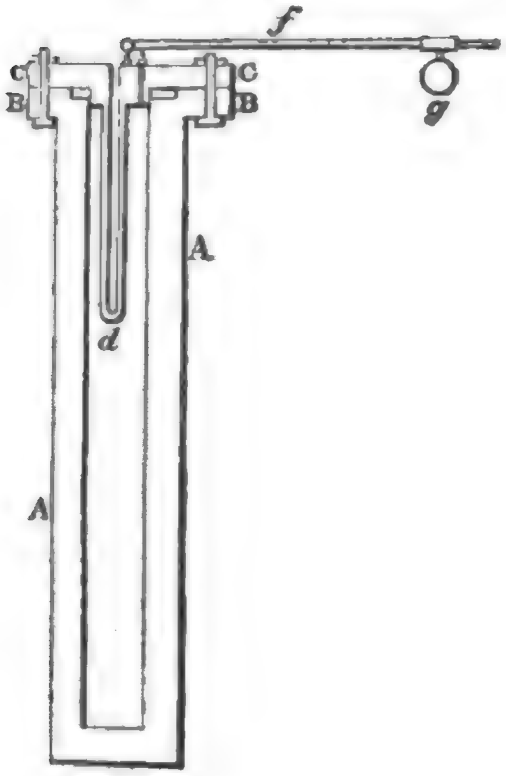
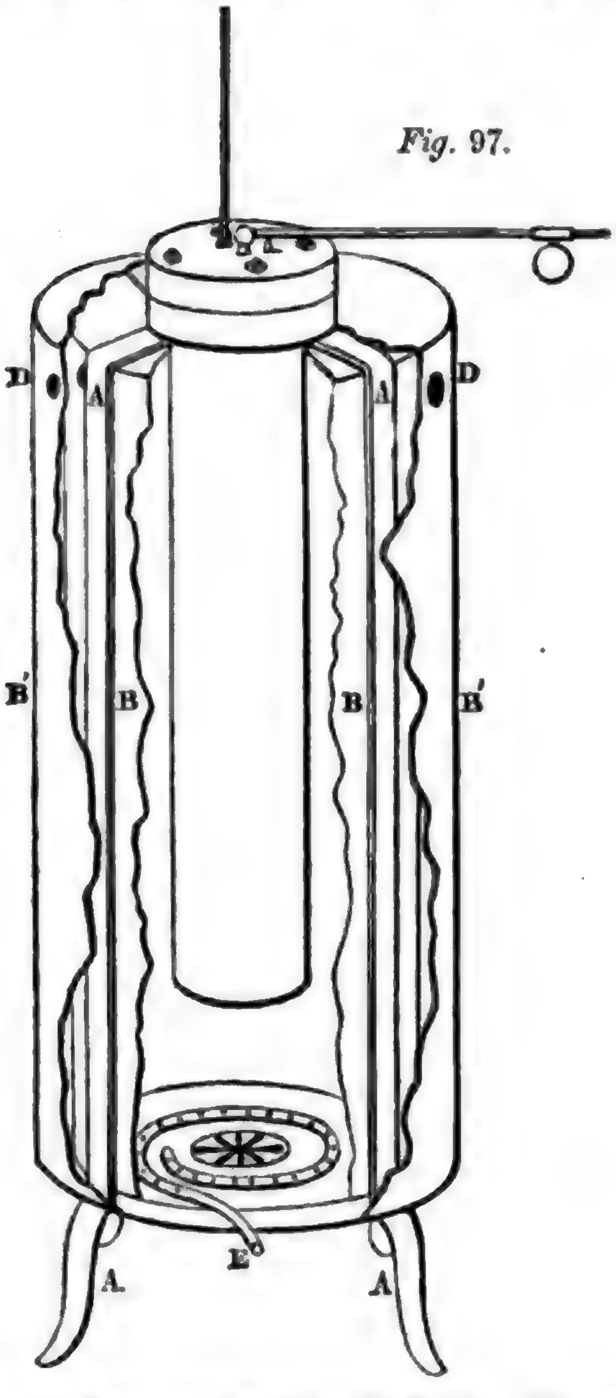


Fig. 97.



A A (*fig.* 96) is an iron cylinder 18½ inches long, 3 inches internal diameter, ⅝ inch thick in the side, and welded in one piece by the steam hammer. This cylinder has a flanch, B B, $1\frac{3}{8}$ inch broad, $\frac{5}{8}$ inch thick, turned true on the upper surface, and having an internal annulus sunk $\frac{1}{20}$th of an inch below the level of the surrounding surface. The cap C C, which is of the same diameter and thickness as the flanch, has a projecting face $\frac{1}{4}$ inch deep which fits exactly into the mouth of the cylinder. Within this projection the cap is pierced with two apertures, into one of which is fitted a cast-iron tube *d*, 6 inches long and $\frac{1}{2}$ inch in external diameter, filled with mercury and destined to receive a thermometer. The other aperture is bouched with brass, and serves as the bed of the safety-valve, which consists of brass wire $\frac{1}{8}$ inch thick, somewhat flattened on two sides, and furnished with a head accurately ground to the surface of the cap. The valve is loaded in the usual way with a lever *f* and weight *g*. The cap and flanch are fastened together by four screw-bolts, which are inserted from below and tightened by a lever-key, and the pressure thus exerted acts upon a lead washer $\frac{1}{8}$ inch thick, placed in the annular depression of the flanch. In this manner the apparatus may be made capable of bearing a pressure of 100 atmospheres without allowing any escape of gas. The cylinder A is about two-thirds filled with water, and the glass tube containing the volatile liquid is enclosed in it. In this manner, tubes of considerable width may be heated without danger of explosion.

The apparatus is heated in a gas-furnace (*fig.* 97). A A A A is a massive frame of wrought-iron, within which is fixed a cylinder B B, cf tin plate, closed at bottom and open at top to receive the apparatus above described. *c* is a regulator for the admission of air. The gas-burner is a copper tube *e*, $\frac{1}{4}$ inch wide and pierced with 18 or 20 apertures. To prevent loss of heat by radiation, the whole apparatus is enclosed in a cylinder B′ B′, of polished tin plate, separated from the inner cylinder by a space about $\frac{1}{2}$ an inch wide. The products of combustion escape by the apertures D D.

BATH-METAL. An alloy of copper and zinc containing a larger proportion of zinc than ordinary brass, and usually prepared by melting brass with zinc.

BATRACHITE. A mineral found on the Rizomberg in the Tyrol, generally massive, with a granular structure, rarely crystalline. It contains according to C. Rammelsberg (Pogg. Ann. li. 466), 37·69 silica, 35·45 lime, 21·79 magnesia, 2·99 protoxide of iron. and 1·27 water. Colour varying from light greenish-grey, like that of a frog (βάτραχος), to white; translucent with waxy lustre. Specific gravity 3·0 to 3·1. Hardness = 5·0. Melts before the blowpipe, assuming a pale red colour with solution of cobalt; is but slightly attacked by acids. The water appears to be unessential, and the composition of the mineral approaches to that of Monticellite. (Handw. d. Chem. ii. 757.)

BATRACHOLEIC ACID. An acid said to be contained, together with stearic acid, glycerin, and a peculiar yellow fat, in the oil obtained by pressure from the epiploon of the water salamander. (Rossignon, Compt. rend. xiii. 929.)

BAUDISSERITE. A dense variety of magnesite containing silica, found near Baudissero in Piedmont. As the amount of water contained in it is very variable, F. v. Kobell and Neumann regard it as a compact hydromagnesite intimately mixed with silica.

BAULITE, or *Krablite.*—A mineral found on the Krabla in Iceland, and likewise on the Baulaberg, either in short prismatic crystals belonging to the triclinic or doubly oblique prismatic system, or in crystallo-granular masses. Cleavage in two directions at right angles to each other. Fracture uneven and conchoïdal. Colourless, with glassy lustre; transparent or translucent. Specific gravity 2·5 to 2·7. Hardness 5·5 to 6·0. In the following table, *a* is the analysis of a specimen of baulite resembling pearlstone, from the Baulaberg, by Forchhammer (Ann. Min. viii. 644); *b* is that of a crystallo-granular variety of baulite, ejected by the volcano of Viti in Iceland, mixed with quartz-crystals and a black needle-shaped mineral, also by Forchhammer (Berzelius's Jahresb. xxiii. 261): *c* is Genth's analysis (J. pr. Chem. lxvi. 93), of crystallised baulite from the Krabla:

	SiO^2	Al^4O^3	Fe^4O^3	Fe^2O	Mn^4O^3	Ca^2O	Mg^2O	K^2O	Na^2O	Cl,	H^2O
a.	74·38	13·78	1·94		1·19	0·85	0·58	2·63	3·57	0·12	2·08
b.	76·65	11·57		0·63		0·05	0·20	3·26	3·73		
c.	80·23	11·34			trace	1·46	trace	4·92	2·26		

These analyses agree sufficiently well with the formula $(M^2O.3SiO^2).(Al^4O^3.6SiO^2)$, which (if $al = \frac{2}{3}Al$) may be reduced to $(M^2al^6)Si^9O^{22}$ or $2R^4SiO^4.7SiO^2$, the formula of an orthosilicate with $\frac{7}{2}$ at. silica; but it is probable, as Bunsen supposes, that the mineral is intimately mixed with orthoclase, Before the blowpipe, baulite is fusible in very thin splinters; with borax and phosphorus-salt it yields clear glasses, a skeleton of silica floating in the latter. It is insoluble in hydrochloric acid. (Handw. d. Chem. ii. 758.)

BAVALITE. See BARALITE.

BAY-SALT. See SODIUM, CHLORIDE OF.

BDELLIUM. A gum-resin of which there are two varieties, *African* and *Indian*. African bdellium is derived, according to Perrotet, from a shrub indigenous in Senegambia, the *Hendelotia africana* (Guillem and Perr); *Balsamadendron africanum* (Arnott); *Amyrès Nicattout* (Adanson), belonging to the amyredaceous order. It forms irregular, translucent masses, of a yellowish, reddish, or brownish colour, according to age; unctuous to the touch, brittle, but soon softening, and growing tough between the fingers. Specific gravity 1·371. It has a bitterish taste, and a moderately strong balsamic odour, not unlike that of myrrh. It does not easily take fire, and when set on fire soon goes out: in burning it gives off a balsamic odour, and sputters a little, owing to the presence of moisture. Alcohol dissolves about ⅗ of it, forming a golden-yellow tincture, from which water throws down a yellowish-white resin, and nitric acid a sulphur-yellow resin. Potash dissolves it completely. By dry distillation it yields ammonia, together with other products. According to Pelletier (Ann. Ch. Phys. [2] lxxx. 38), it contains 59 per cent. resin, 9·2 gum, 30·6 vegetable mucus, and 1·2 volatile oils (and loss).

The resin is transparent, but becomes white and opaque by boiling with water; melts between 58° and 60° C. According to Johnston (J. pr. Chem. xxvi. 145), it is $C^{40}H^{31}O^{5}$. The gum is yellowish-grey, and when treated with nitric acid, yields malic but no mucic acid. The vegetable mucus is also yellowish-grey, swells up with water, coagulates with alcohol, and is converted by nitric acid into a thin liquid. The volatile oil is heavier than water.

Indian bdellium is said to be obtained from *Balsamodendron Mukal* (Hooker), also an amyredaceous tree, growing in Scinde. It forms irregular, greenish-brown, or blackish masses, having a strong odour, and sharp bitter taste like myrrh. It becomes sticky between the fingers.

BEAN. Two species of bean are commonly cultivated in Europe, viz. 1. *Faba vulgaris*, or *Vicia Faba*, the common field or garden bean (*Feldbohne*, *grosse Bohne*, *Saubohne*), the most common garden varieties of which are the Windsor broad bean, the Toker, the long-pod, and the Mazagan, while for field cultivation, the Heligoland, or tick-bean, and the common horse-bean, are preferred as being more hardy.—2. *Phaseolus vulgaris*, the French, haricot, or kidney-bean, innumerable varieties of which are cultivated, some dwarf, others climbing. The scarlet-runner, *Phaseolus multiflorus* is closely allied to this species.

The seeds of these several species and varieties differ but little in chemical composition, as the following tables will show; but they are all remarkable for the large amount of nitrogenous matter (legumin) and phosphoric acid which they contain.

TABLE A.—*Composition in* 100 *parts of various kinds of Bean.*

	Legumin, &c.	Sugar.	Gum.	Starch.	Fat.	Pectin substances.	Woody fibre.	Ash.	Water.
1. Field-bean (*air-dried*)	24·2	—	44·2		1·4	—	12·6	3·6	14·0
2. " "	23·3	2·0	4·5	36·0	2·0	4·0	10·0	3·6	14·8
3 Haricot-bean	25·0	0·3	4·0	38·0	3·0	12·0		3·7	14·0
4. " old Irish (*undried*)	24·7	4·6		36·4	2·4	17·6*		1·8	12·8
5. " Egyptian (*undried*)	24·6	6·5		31·5	2·8	18·8			10·8
6. " common white (*air-dried*)	22·8	45·4			2·7	6·2 †		1·8 3·6	19·3

1. Poggiale (J. Pharm. [3] xxx. 180). The shells amounted to 15 per cent. of the weight of the entire pods, and contained neither legumin nor starch.—2. Mean of earlier analyses by Braconnot, Horsford, and Krocker.—3. Mean of earlier analyses by Einhof, Boussingault, Horsford, and Krocker.—4, 5. Polson (Chem. Gaz. 1855, p. 211).—6. Poggiale (*loc. cit.*) The shells amounted to 7·5 per cent. of the weight of the entire pods, contained very little starch, 0·2 per cent. fat, 6·5 nitrogenous matter, and 5·8 ash.

Ward and Eggar (Jahresber. d. Chem. 1849, p. 708), obtained from several varieties of fresh beans grown on various soils: 2·4 to 3·6 per cent. nitrogen, 1·2 to 1·7 per cent. fat, and 11·0 to 17·0 per cent. water.—Way and Ogston obtained from the same varieties of bean (Heligoland and Mazagan), grown on various soils, in 100 pts. of the fresh seeds: 8·1 to 17·0 per cent. water, and in 1000 pts. of the dried seeds of five varieties, 2·5 to 2·9 per cent. sulphur, in a sixth kind, 4·6 per cent. sulphur.

* Cellulose and Shells.

† Cellulose.

Mayer (Ann. Ch. Pharm. ci. 144), obtained from 100 pts. of air-dried Mazagan beans, 11·8 to 12·5 per cent. water, 1·13 and 1·18 phosphoric anhydride, and 4·25 to 4·3 nitrogen. In dwarf haricot beans, he found 10·1 per cent. water, 1·06 phosphoric anhydride, and 3·32 nitrogen; in climbing haricot beans, 9·4 per cent. water, 0·95 phosphoric anhydride, and 3·17 nitrogen.

The sugar occurring in beans is usually regarded as grape-sugar. Vohl (Ann. Ch.

TABLE B.—*Composition* (in 100 pts.) *of*

	Potash, K^2O.	Soda, Na^2O.	Lime, Ca^2O.	Magnesia, Mg^2O.
I. SEED.				
Faba vulgaris.				
1. Common field bean from Holland . . .	20·8	17·8	7·3	8·9
2. " " " Alsace	46·3	—	5·3	9·0
3. " " " Giessen . . .	33·9	13·0	4·9	6·3
4. " " " England . . .	51·7	0·5	5·2	6·9
5. Mazagan bean (seed sown)	36·7	0·1	12·1	6·0
6. raised therefrom on clay soil	43·4	1·3	5·8	5·7
7. " " sandy soil . . .	45·7	—	13·3	6·5
8. Heligoland bean (seed sown)	42·9	1·6	7·7	7·7
9. raised therefrom on clay soil . . .	43·5	2·4	4·8	5·6
10. " " sandy soil . . .	40·7	—	8·2	7·7
Phaseolus vulgaris.				
11. Haricot bean from Worms	38·9	11·3	5·9	9·0
12. " " Alsace	51·0	—	6·0	11·9
13. " " Kurhessen	22·1	21·4	5·5	7·5
14. " " England	36·8	18·4	7·7	6·3
II. STRAW.				
15. Common field bean	15·3	13·3	39·3	7·1
16. " "	32·8	2·8	19·8	2·5
17. Mazagan bean on clay soil	18·7	13·9	18·9	3·1
18. " " sandy soil	25·6	4·1	22·4	4·7
19. Heligoland bean on clay soil	19·6	—	18·3	4·9
20. " " sandy soil	21·1	0·2	25·6	6·9

1. Analysed by Bichon (Handw. d. Chem. 2te Aufl. ii. [2], 259).—2. Boussingault (*ibid.*)—3. By Büchner (*ibid.*)—4–10 and 16–20. Way and Ogston (Journal of the Royal Agricultural Society, ix. pt. 1).—11. Levi (Handw.)—12. Boussingault (*ibid.*)—13. Thon (*ibid.*)—14. Richardson (Jahresber. f. Chem. 1847, 1848, p. 1075, Tafel C).—15. Hertwig (Handw.) This contained carbonic acid, which has been deducted.

The pods of *Phaseolus multiflorus* contain, according to T. J. Herapath (Chem. Soc. Qu. J. 4), 94·1 per cent. water; air-dried, they yielded 0·631 per cent., and, after drying at 100° C., 10·7 per cent. of ash, containing:—

Of matter soluble in water: 14·1 carbonic anhydride; 3·4 sulphuric anhydride; 1·5 phosphoric anhydride; 36·1 potash; 4·9 chloride of sodium.

Of matter insoluble in water: 22·2 carbonate of calcium; 3·8 carbonate of magnesium; 11·9 phosphate of calcium; and 2·1 silica.

BEAUMONTITE. A mineral found in the gneiss at Jones Falls near Baltimore, in North America, in square pyramids, having terminal dihedral angles of 147° 28′, and the lateral edges replaced by the square prism ∞ P.

Cleavage parallel to ∞ P. Yellowish-white to honey-yellow, translucent, with nacreous lustre. Specific gravity 2·24. Hardness 4·5 to 5·0. According to Delesse (Ann. Ch. Phys. [3] ix. 385), it contains 64·2 silica, 14·1 alumina, 4·8 lime, 1·7 magnesia, 1·2 protoxide of iron, 0·6 soda (and loss), 13·4 water. Alger and Dana are of opinion that the mineral thus characterised is merely stilbite, the form of which has been incorrectly determined, and the analysis made with impure material.

Pharm. xcix. 125), found, in the unripe seeds, another kind of sugar, which he at first regarded as a peculiar substance, designated by him as *phaseomannite*, from its resemblance to mannite. According to later investigations, however, it appears to be identical with inosite, the saccharine substance which Scherer obtained from muscular flesh.

the Ash of Bean Seed and Bean Straw.

Sesquioxide of iron, Fe^2O^3.	Sulphuric anhydride, SO^3.	Silica, SiO^2.	Carbonic anhydride, CO^2.	Phosphoric anhydride, P^2O^5.	Chloride of potassium, KCl.	Chloride of sodium, NaCl.	Ash per cent.	
							In substance undried.	In substance dried at 100° C.
1·0	1·3	2·4	—	38·0	—	2·4		
—	1·6	0·5	1·0	35·7	1·5			
0·7	—	0·5	—	40·5				
trace	3·0	0·4	3·4	28·7	—	—	2·37	2·65
0·6	4·3	1·5	1·6	33·7	—	3·2	2·85	3·43
0·1	3·1	0·4	3·4	36·7	—	—	2·68	3·01
0·6	3·1	0·4	0·8	26·9	0·9	1·8	2·48	2·97
0·3	5·1	2·2	2·6	29·9	—	—	2·54	2·90
0·1	6·2	0·7	2·8	30·6	—	3·2	2·53	2·94
0·3	5·3	0·04	0·3	33·3	1·2	3·2	2·80	3·83
0·1	2·5	0·4	—	31·3	—	0·5		
—	1·3	1·0	3·3	28·4	0·2			
0·3	2·3	1·5	—	35·9	—	3·4		
2·8	4·0	4·1	—	17·0	—	2·8	0·68	
2·0	2·1	11·3	—	12·1	—	0·4		
0·6	1·4	2·6	25·3	0·5	—	11·5	4·97	5·56
0·7	1·4	2·2	24·4	6·5	—	10·0	5·17	5·81
0·5	5·4	4·6	22·6	3·3	—	6·9	4·64	5·05
0·4	3·9	1·5	25·7	11·1	3·6	11·0	6·47	7·24
2·0	2·1	7·3	18·1	8·4	—	8·3	6·05	6·69

The name *Beaumontite* is also given by Jackson to a variety of siliceous malachite, or an allied mineral containing silica, water, and oxide of copper.

BEBIRIC ACID. An acid contained, according to Maclagan, in the bark of the *Bebeeru* or *Sipeeri* (*Nectandra Rodiei*), a tree growing in British Guiana. To obtain the acid, the bark is exhausted with water acidulated with acetic acid; the alkalis, bebirine and sepirine, with which the acid is in combination, are precipitated by ammonia; the filtered liquid is precipitated by acetate of lead; the precipitate decomposed by sulphuretted hydrogen; the clear liquid evaporated over sulphuric acid; and the residue digested in ether, which dissolves the acid, but leaves the colouring matter. On evaporating the ethereal solution, bebiric acid remains as a white crystalline substance, having a waxy lustre. By exposure to the air, it is gradually reduced to a syrupy liquid. It melts a little above 200° C., and sublimes in tufts of needles. With potash and soda, it forms deliquescent salts soluble in alcohol; sparingly soluble salts with the alkaline earths; the lead-salt also is but sparingly soluble in alcohol.

BEBIRINE or **BEBEERINE.** $C^{19}H^{21}NO^3$ or $C^{38}H^{21}NO^6$.—An alkaloid discovered in 1834 by Dr. Rodie of Demerara, in the bark of the bebeeru tree (*vid. sup.*). Maclagan in 1843 (Ann. Ch. Pharm. xlviii. 106), showed that Rodie's bebirine was a mixture of two distinct alkaloids, which he denominated *bebirine* and *sepirine*. The former of these was more exactly investigated in 1845 by Maclagan and Tilley (Phil. Mag. xxvii. 186), who assigned to it the formula $C^{35}H^{20}NO^6$. But bebirine was first obtained perfectly pure by v. Planta (Ann. Ch. Pharm. lxxvii. 333), who assigned to it the formula above given.

Preparation.—1. The bark is exhausted with water containing sulphuric acid; the extract is concentrated, filtered, and precipitated by ammonia; and the precipitate, consisting of bebirine, sepirine, and tannin, is dried, dissolved in acidulated water, and decolorised with animal charcoal. The solution again decomposed by ammonia, yields a nearly colourless precipitate of bebirine and sepirine. As, however, the treatment with animal charcoal always occasions a certain loss of alkali, it is better to triturate the precipitate while yet moist with oxide of lead or milk of lime, dry the mixture over the water-bath, extract the two alkaloids by means of alcohol, and evaporate the alcoholic solution. To separate the two alkaloids, the product is exhausted with ether, which dissolves only the bebirine (Maclagan and Tilley). — 2. The bebirine prepared by the process just described, is not quite pure, and does not dissolve completely in ether. It may be purified by treating it with acetic acid, adding acetate of lead to the filtrate, precipitating the mixture with caustic potash, washing the precipitate with a large quantity of cold water, and redissolving in ether. The ethereal solution, when evaporated, leaves the bebirine in the form of a clear yellow syrup, which is dissolved in a small quantity of strong alcohol, and the solution is added drop by drop to a considerable quantity of water, with constant agitation: bebirine then separates in the form of a floculent precipitate. (v. Planta.)

Bebirine when dry, is a white, amorphous, odourless powder, which does not change by exposure to the air, and becomes electrical by friction. It melts at 198° C. to a vitreous mass, which decomposes at a higher temperature. — By boiling with strong nitric acid, it is converted into a yellow pulverulent substance. Heated with chromic acid, it yields a black resin. It does not yield chinoline when heated with caustic potash.

Bebirine is nearly insoluble in water, but dissolves readily in alcohol and ether, especially with the aid of heat. The solution has an alkaline reaction, and a very persistent bitter taste. It dissolves readily in acetic and hydrochloric acid, forming bitter uncrystallisable salts. It is precipitated from its solutions by dilute nitric acid.

Hydrochlorate of bebirine is very soluble in water; and the solution treated with caustic alkalis or their carbonates yields bebirine in white flakes, easily soluble in excess of the reagents. The *chloromercurate* is obtained by adding mercuric chloride to the solution of the hydrochlorate; a small quantity of hydrochloric acid or chloride of ammonium increases the precipitate; but an excess redissolves it. The *chloroaurate* is a brown-red precipitate. The *chloroplatinate*, $C^{19}H^{21}NO^{3}.HCl.PtCl^{2}$, is an orange-yellow amorphous precipitate, insoluble in hydrochloric acid. The *sulphocyanate* is a white precipitate; the *picrate* yellow.

Sulphate of bebirine in the impure state has been used as a remedy in intermittent fever.

The bark of the bebeeru tree, which has a bitter and astringent taste, contains about 2·5 per cent of bebirine and sepirine, together with bebiric acid and a peculiar tannin; the seed contains the same principles, together with about 50 per cent. of starch, which impedes the extraction of the bases and acid.

BECKITE. This name has been given to a mineral from Paynton in Devonshire, which, according to Kenngott, is merely a coral hardened into a chalcedonic or hornstone variety of quartz, intergrown with compact grey limestone.

BEECH. *Fagus sylvatica.*—Beech-wood recently felled, has a specific gravity of 0·982, and contains 40 per cent. water; after drying in the air, it has a specific gravity of 0·590, and contains 18 to 20 per cent. water. After drying at 100° C. it contains, according to Baer (Arch. Pharm. [2] lvi. 159), 46·1 to 48·3 per cent. carbon, 5·8 to 6·0 hydrogen, 46·6 to 45·1 oxygen, and 1·2 to 0·6 ash. According to Chevandier (Compt. rend. xxiv. 269), it contains 49·8 per cent. C, 6·0 H, 43·1 O, 1·1 N, and yields 1·06 per cent. ash. According to Sprengel (J. techn. Chem. xiii. 384), the air-dried wood yields 0·365 per cent. ash, containing 0·14 crude carbonate of potash; and the leaves which fall in autumn yield 6·695 per cent. ash.

The following table exhibits the composition per cent. of the ash of beech-wood, and of the leaves. *a*, *g*, *h* are by Sprengel (*loc. cit.*); *b*, *c* (Witting, Pharm. Centr. 1851, 104); *b*, of wood grown on sandstone (*bunter Sandstein*), near Marburg; *c* of wood grown on the Muschelkalk, near Morschen in Kurhessen; *d*, *e*, *f* (Heyer and Vonhausen, Ann. Ch. Pharm. lxxxii. 180). The wood was grown on a basaltic hill near Giessen. A hectare of surface produced yearly 2·672 cubic metres of stem-wood (*Scheitholz*); 0·965 c. m. large branch-wood (*Prügelholz*); 0·769 c. m. small branch-wood (*Stockholz*); and 1·878 c. m. of twigs (*Reisholz*); and these quantities of wood extracted from the soil, in all, 51·3 kilogrammes of ash, viz. the stem-wood 17·0 kil., the large branch-wood 9·9 kil., the small branch-wood 4·9 and the twig-wood 19·5 kil. Hence a cubic metre of the stem-wood yields 6·342 kilogrammes of ash; of large branch-wood 10·233 kil.; and of twig-wood 14·144 kil. The table shows also that, reckoning from the bottom upwards, the proportion of *alkali* diminishes, that of the *phosphoric* and *sulphuric acid* increases; while of *silica*, the twigs have more than the stem, and the thick branches least of all.

	Wood.			Wood with Bark.			Leaves.	
				Stem.	Large Branches.	Twigs.		
	a	*b*	*c*	*d*	*e*	*f*	*g*	*h*
Potash	24·9	10·9	6·9	13·1	12·5	11·8	—	5·1
Soda	1·1	1·2	0·3	3·1	1·7	1·8	0·7	1·0
Lime	27·4	13·5	43·6	39·8	37·8	40·2	51·7	37·7
Magnesia	6·6	12·0	5·4	10·1	13·4	9·0	6·1	7·9
Alumina	2·2	0·05	—	—	—	—	1·1	
Ferric oxide	—	—	0·6	0·5	0·3	0·6	0·8	0·4
Manganic oxide	7·4	3·4	trace	0·9	1·0	0·6	4·1	2·4
Sulphuric anhydride	7·1	1·0	0·6	0·4	0·5	1·0	1·9	1·3
Silica	5·2	6·3	2·1	6·2	5·5	8·2	27·0	28·5
Carbonic anhydride	—	26·2	28·3	19·6	17·4	16·3	—	10·5
Phosphoric	—	5·6	7·5	6·0	9·6	10·3	6·6	4·8
Ferric phosphate	15·1							
Chloride of sodium	2·6	6·7	0·6	0·1	0·8	0·1	—	0·3
Charcoal	—	2·1						
Sand	—	10·7	3·7					

The *bark* of the beech contains, together with the usual constituents of vegetable substances, about 2 per cent. of tannin, also a peculiar red substance, and another which smells like vanilla. The latter is soluble in alcohol, insoluble in water and in ether; and by shaking up the alcoholic solution with hydrate of lead, and repeated precipitation by water, it may be obtained as an amorphous white powder, with an odour of vanilla and a bitter taste. It dissolves in acetic acid and in alkalis; nitric acid converts it into oxalic acid. (Lepage, J. Pharm. [3] xii. 181.)

Dry beech-bark yields about 0·6 per cent. crude potash. According to Hertwig (Ann. Ch. Pharm. xlvi. 97), it yields 6·6 per cent. ash, containing in 100 pts. 3·0 soluble salts, consisting of alkaline carbonates, sulphate of potassium, and a trace of chloride of sodium, and 97·0 pts. of insoluble salts, viz. 64·7 carbonate of calcium, 16·9 magnesia, 2·7 phosphate of calcium, 1·9 phosphates of magnesium, aluminium, and iron, and 9·0 silica.

The *ash of beech-nuts* yields in 100 pts. 18·1 K^2O, 7·5 Na^2O, 19·5 Ca^2O, 9·2 Mg^2O, 2·5 Mn^2O^2, 16·5 P^2O^5, 0·7 NaCl. 1·5 SiO^2, 9·1 CO^2, and 9·4 charcoal. (Handw. d. Chem. 2te Aufl. ii. [2] 549.)

BEECH-NUT OIL. *Huile de faine.* $C^{15}H^{28}O^2$.—Beech-nuts yield, by pressure, about 17 per cent. of a clear, light-yellow, viscid oil, inodorous, having a mild taste and a density of 0·9225 at 15° C. It solidifies at 17° C., and is coloured rose-red by nitric acid. It is a non-drying oil, and yields a white soap. It is used in cooking and for illumination. Mixed with eight or ten times its bulk of water, and treated at 60° or 80° C. with *chlorine* gas, it is converted into a chlorinated oil containing $C^{15}H^{26}Cl^2O^2$. *Bromine* acts on it with violence, but if the oil be cooled at the same time, the compound $C^{15}H^{26}Br^2O^2$ is produced. (Lefort, Compt. rend. xxxv. 734.)

BEER is the wine of grain, and is prepared from malt, or grain, generally barley, which has been allowed to germinate. The grain is steeped for two or three days in water, until it swells, becomes somewhat tender, and tinges the water of a bright reddish-brown colour. The water being then drained away, the barley is spread about two feet thick upon a floor, where it heats spontaneously, and begins to grow by first shooting out the radicle. In this state, the germination is stopped by spreading it thinner, and turning it over for two days; after which it is again made into a heap, and suffered to become sensibly hot, which usually happens in little more than a day. Lastly, it is conveyed to the kiln, where, by a gradual and low heat, it is rendered dry and crisp. This is malt, and its qualities differ according as it is more or less soaked, drained, germinated, dried, and baked.

Malt is distinguished by its colour, as pale, amber, brown, or black malt, according to the different degrees of heat to which it has been subjected. Pale malt is produced when the drying temperature does not exceed 90° to 100° F., amber-coloured malt when the heat has been raised to 120° to 125°, and brown malt at 150° to 170°. Black malt, commonly called patent malt, is prepared by roasting in cylinders like coffee, at a heat of 360° to 400° F.; it is used as colouring matter in the brewery of porter.

Indian corn, and probably all large grain, requires to be suffered to grow into the blade, as well as root, before it is fit to be made into malt. For this purpose, it is buried about two or three inches deep in the ground, and covered with loose earth; and in ten or twelve days it springs up. In this state, it is taken up and washed, or fanned, to clear it from dirt; and then dried in the kiln for use.

During the process of germination, the albuminous matter of the barley or other grain is brought into the peculiar state called *diastase*, in which it acts as a ferment on the starch contained in the grain, converting it into dextrin and sugar, and thereby rendering it soluble. A portion of the starch is, however, always left unchanged by the germinating process, and its conversion into dextrin and sugar is completed by the kiln-drying. The benefit of this latter process is, therefore, not confined to the mere expulsion of moisture from the grain; indeed kiln-dried malt always yields a larger quantity of saccharine extract than malt which has been left to dry in the air at ordinary temperatures.

The diastase of malt is capable of converting into sugar a much larger quantity of starch than that which the grain itself contains: hence in the preparation of the extract, the malt may be mixed with a certain quantity of unmalted barley or other grain. In Belgium, large quantities of beer are prepared from malt mixed with potato starch.

To make beer, the malt, after being ground or cut to pieces in a mill, is placed in a tun or tub with a false bottom; water at about 180° F. is then poured upon it; and the whole is well stirred about by suitable machinery. This operation is called *mashing*. After the infusion has been left for a few hours to clarify or *set*, the clear liquor or *sweet wort* is transferred to a copper boiler and boiled with hops, which give it a bitter aromatic taste, and perhaps also render it less liable to spoil by keeping. When the wort has been sufficiently boiled, it is drawn from the copper into large shallow vessels, so as to cool it as rapidly as possible to the temperature of the air, and thereby avoid an irregular acid fermentation, to which it would otherwise be liable. It is then transferred to the fermenting vats, which in large breweries are of great capacity, and mixed with yeast, the product of a preceding operation. The liquid is thereby brought into a state of commotion; the sugar is more or less converted into alcohol and carbonic acid, which escapes as gas; and the nitrogenous matter of the extract is converted into yeast, part of which is expended in keeping up the fermentation, while the rest rises to the surface. The fermentation is never suffered to run its full course, but is always stopped at a certain point, by separating the yeast and drawing off the beer into casks. A slow and almost insensible fermentation then takes place, whereby more of the sugar is converted into alcohol, and the beer is rendered stronger and less saccharine.

During this last process, the beer gradually becomes clear or fine, the solid particles of yeast which float about in it during the fermentation, and render it muddy, being gradually brought to the surface and discharged through the bung-holes of the casks, whence the yeast is conveyed into proper receptacles. A very effective arrangement for this purpose is adopted at the extensive breweries of Messrs. Bass and Allsopp at Burton-on-Trent, for a description and figure of which see *Muspratt's Chemistry*, vol. i. p. 276. Frequently, however, it is found necessary to assist the clarification by means of substances called *finings*, which lay hold of the suspended matter, and precipitate it to the bottom. Isinglass dissolved in sour beer is often used for this purpose, also gelatin, white of egg, serum of blood, Carragheen moss, and the dried stomach of the cod, called *sounds*. It is best, however, when the clarification takes place spontaneously, without the use of finings; for all these substances tend to make the beer flat, and prevent it from carrying a good head. The composition of the water used in brewing has a great influence on the result. Lime in particular appears to favour the clarification, by combining with the acids of the malt-extract, and forming insoluble salts, which carry down the suspended matter. The spring-water of Burton-on-Trent (not that of the river Trent) contains 19 per cent. of sulphate of lime, only a small portion of which is precipitated on boiling.

The strength and taste of beer are susceptible of endless variety, according to the quality and quantity of the malt and hops used, and the mode of conducting each stage of the process, but especially the fermentation. If the first fermentation be stopped at an early stage, the beer will contain a considerable quantity of sugar and comparatively little alcohol: it will be mild, and if bottled, will acquire the property of effervescing strongly when the bottle is opened, because the carbonic acid produced by the subsequent slow fermentation, remains dissolved in the liquid, and escapes with violence as soon as the pressure is removed. If, on the other hand, the fermentation be allowed to go on in the vat or in casks, till nearly all the sugar is converted into alcohol and the carbonic acid escapes, the beer then becomes more alcoholic; but if the process be allowed to go on too long, it loses its briskness and becomes flat and unpalatable. *Strong* beers are those which contain a considerable amount of alcohol; *substantial* beers are those which are rich in malt-extract; the latter are also said to possess *body*.

The malt-liquors consumed in this country are of two kinds, Ale and Porter. Ale is prepared from the paler kinds of malt, and in its preparation, the first fermentation is checked at such a stage as to leave a considerable quantity of saccharine matter in the liquor, which, by its subsequent conversion into alcohol and carbonic acid, may keep up the briskness. The ale is mild or bitter, according to the quantity of hops added to the wort. *Pale ale* is prepared from the palest malt dried in the sun or by steam heat, and from the best and palest hops. An essential point in its preparation is to keep the fermenting temperature as low as possible, never allowing it to rise above 72° F. By this means, the formation of acetic acid is prevented, as also the solution of the yeast by alcohol, which always communicates an unpleasant flavour to the liquor,—and the delicate flavour and aroma of the hop are preserved. *Scotch ale* is a sweet strong ale; it was formerly flavoured with honey, but that practice appears to be now abandoned.

Porter is a dark-coloured beer, prepared from a mixture of pale, amber, brown, and black malt. The following table (taken from Muspratt's Chemistry) exhibits the composition of the various mixtures employed:

Table of Porter Grists.

No.	Black.	Brown.	Amber.	Pale.	Total.
1	9	0	0	91	100
2	6	34	0	60	100
3	2	30	10	58	100
4	3	25	15	57	100
5	4	24	24	48	100
6	5	0	95	0	100

Of these the preference is given to the last two; in the others, the excess of black and brown malt introduces too much carbonaceous and useless matter, whence the porter acquires a disagreeable taste, as if liquorice were added to it. The fermentation of porter in the vats is carried on till the original gravity of the liquid is reduced to about one-third. *Stout* is merely a stronger kind of porter. *Small beer*, as its name implies, is a weaker liquor, and is made either by adding a large quantity of water to the malt, or by mashing with a fresh quantity of water, the residuum left after ale or porter has been drawn off.

The temperature at which the fermentation of beer is conducted, has a marked effect on its quality, and especially on its power of keeping without turning sour. When the fermenting temperature ranges from 65° to 90° F., as is the case with the beers of England, France, Belgium, and most parts of Germany, the beer gradually becomes sour by contact with the air, the alcohol being slowly converted into acetic acid. But Bavarian beer, which is fermented at a much lower temperature, 8° or 10° C. (46·5 to 50° F.), does not undergo this change. The difference arises from the manner in which the fermentation takes place, and is explained by Liebig as follows: Wort is proportionally richer in soluble gluten than in sugar, and when set to ferment in the ordinary way, it evolves a large quantity of yeast in the state of a thick froth, with bubbles of carbonic acid gas adhering to it, whereby it is floated to the surface of the liquid. Now the conversion of gluten into yeast is partly, at least, a process of oxidation; and when the liquor is covered with a thick scum, as just described, the gluten still dissolved in the liquid, not having free access to the air, appears to take oxygen from the sugar and other matters contained in the liquid, the formation of the yeast thus going on at the expense of the sugar, which is consequently destroyed before the whole of the gluten is converted into yeast. From this cause, a quantity of free gluten is left in the liquid, and on subsequent exposure to the air, this gluten acts as a ferment, inducing the conversion of the alcohol into acetic acid. In the Bavarian process, on the contrary, the carbonic acid, instead of escaping in large bubbles, which, carry the yeast to the surface, rises in minute bubbles in the same manner as from an effervescing mineral water; little or no scum forms on the surface, but the yeast, as it is produced, sinks to the bottom, and leaves the surface of the wort freely exposed to the air. The gluten is thus converted into yeast by atmospheric oxidation, and is at last wholly removed from the liquid without decomposition of the sugar. Beer thus fermented, is not liable to acidification by exposure to the air.

The kind of fermentation last described, is called *bottom fermentation* (*Untergahrung*), and the yeast produced by it *bottom yeast* (*Unterhefe*); while the ordinary fermentation process is called *top fermentation* (*Obergahrung*), and the yeast which it produces *top yeast* (*Oberhefe*). These two kinds of yeast differ essentially in their properties and mode of action. The top-yeast is gluten oxidised in a state of putrefaction, and the bottom yeast is the gluten oxidised by *eremacausis* or slow combustion. Each of them has a tendency to induce the particular kind of fermentation by which it was itself produced. (See FERMENTATION.)

For further details respecting the preparation and properties of beer, see the articles BEER and BREWING in the new edition of *Ure's Dictionary of Arts, Manufactures, and Mines;* also the article BEER in *Muspratt's Chemistry*, and in the *Handwörterbuch der Chemie*, 2te Aufl. ii. [1] 103·6

ANALYSIS OF BEER.—The normal constituents of beer are alcohol, carbonic acid, and extractive matters of malt and hops; acetic acid is also present, but its amount in good beer is very small.

The amount of carbonic acid in beer is but small, not exceeding 0·1 to 0·5 per cent. even in bottled beer, and of this small quantity the greater portion escapes as soon as the beer is opened. The strength of the frothing will give a very good idea of its relative amount. An exact estimation of the carbonic acid is indeed seldom necessary; but if desired, it may be made by boiling a known quantity of the beer in the flask-apparatus, represented in *fig.* 5, p. 119, (art. ALKALIMETRY.) The carbonic acid (anhydrous) then escapes as gas, while the vapours of water and alcohol given off at the same time are retained by the chloride of calcium in the drying tube.

The amount of acetic acid is estimated by the usual processes of ACIDIMETRY (*q. v.*)

The quantity of extractive matter in beer may be determined by evaporating 20 grammes of beer in a platinum or porcelain dish, and drying the residue in an air-bath (p. 520) at 100°—115° C. till it ceases to lose weight. Before weighing, it must be cooled under a bell-jar over chloride of calcium, as it is very hygroscopic.

It is seldom necessary to examine the extractive matter any further. It consists mainly of sugar, dextrin, albuminous matter, and lupulin, the bitter principle of the hop. The amount of dextrin and sugar may be determined by moistening the dried residue with water to a thin syrup, and gradually adding strong alcohol as long as dextrin is thereby separated. The clear sugar-solution may then be decanted, and the dextrin freed from the remaining sugar by repeated solution in water and precipitation by alcohol. The solutions of dextrin and sugar may then be evaporated to dryness, and the residues weighed. The albuminous matter may be estimated from a separate portion of the beer by boiling it so as to coagulate the albumin, collecting the precipitate on a tared filter, then washing, drying, and weighing it. Lastly the sum of the weights of the dextrin, sugar, and albuminous matter, deducted from the total weight of the extract gives the quantity of lupulin.

The inorganic constituents of beer are estimated by evaporating to dryness a known quantity of the beer, charring the residue, and then igniting it, as in the preparation of plant-ashes (p. 419). They consist chiefly of the phosphates of calcium and magnesium. Alkaline phosphates may likewise be found, but the greater part of them is dissolved out during the maceration of the barley for malting. Common salt, which is sometimes added to beer, will of course be found in the ash. Any considerable amount of alkaline carbonate may be attributed to alkali added to neutralise free acid in the beer.

The amount of alcohol in beer is ascertained by distilling 500 to 1000 grammes (15 to 30 ounces) in a somewhat capacious retort, having its neck inclined upwards and connected with a Liebig's condenser, receiving the distillate in a tared flask, weighing it, and determining its specific gravity at $15\frac{5}{9}$ C. (60° F.), that of water at the same temperature being assumed = 1·000; or the proportion of alcohol may be found by testing the distillate with a delicate alcoholometer. The weight per cent. of alcohol is then found by means of table A, which is an amplification of part of that given under ALCOHOLOMETRY (p. 81), and thence the total amount of alcohol in the given quantity of beer may be found.

Suppose, for instance, 1000 grms. of beer gave 615·38 grms. of distillate of specific gravity 0·98949 at 60° F.; then, according to the table, the distillate would contain 6·11 per cent. alcohol, and therefore the 615·38 grms. of distillate would contain 37·6 grms. alcohol. Now these 37·6 grms. of alcohol were obtained from 1000 grms. of beer; consequently the amount of alcohol in the beer is 3·76 per cent. The trouble of calculation may be saved by diluting the distillate till its weight becomes equal to that of the beer employed; the specific gravity will then at once give the percentage by weight of alcohol in the beer. If, for example, the distillate after dilution exhibited a specific gravity = 0·9932, the percentage of alcohol would be 3·76. If a Tralles' alcoholometer were used, it would show in the distillate, before dilution, a percentage by volume of 7·6, corresponding to 6·11 by weight. In using the alcoholometer, it is best not to dilute the distillate, unless the instrument is especially graduated for very weak liquids. If the observed specific gravity or alcoholometer-degree does not occur in the table, the weight per cent. of alcohol will be found by interpolation.

TABLE A.—*Specific Gravity and Strength of Spirits.*

Volume per cent.	Weight per cent.	Specific Gravity.	Volume per cent.	Weight per cent.	Specific Gravity.
1·	0·80	0·99850	4·5	3·60	0·99350
1·1	0·88	0·99835	4·6	3·68	0·99336
1·2	0·96	0·99820	4·7	3·76	0·99322
1·3	1·04	0·99805	4·8	3·84	0·99308
1·4	1·12	0·99790	4·9	3·92	0·99294
1·5	1·20	0·99775	5·0	4·00	0·99280
1·6	1·28	0·99760	5·1	4·08	0·99267
1·7	1·36	0·99745	5·2	4·16	0·99254
1·8	1·44	0·99730	5·3	4·24	0·99241
1·9	1·52	0·99715	5·4	4·32	0·99228
2·0	1·60	0·99700	5·5	4·40	0·99215
2·1	1·68	0·99686	5·6	4·48	0·99202
2·2	1·76	0·99672	5·7	4·56	0·99189
2·3	1·84	0·99658	5·8	4·64	0·99176
2·4	1·92	0·99644	5·9	4·72	0·99163
2·5	2·00	0·99630	6·0	4·81	0·99150
2·6	2·08	0·99616	6·1	4·89	0·99137
2·7	2·16	0·99602	6·2	4·97	0·99124
2·8	2·24	0·99588	6·3	5·05	0·99111
2·9	2·32	0·99574	6·4	5·13	0·99098
3·0	2·40	0·99560	6·5	5·21	0·99085
3·1	2·48	0·99546	6·6	5·30	0·99072
3·2	2·56	0·99532	6·7	5·38	0·99059
3·3	2·64	0·99518	6·8	5·46	0·99046
3·4	2·72	0·99504	6·9	5·54	0·99033
3·5	2·80	0·99490	7·0	5·62	0·99020
3·6	2·88	0·99476	7·1	5·70	0·99008
3·7	2·96	0·99462	7·2	5·78	0·98996
3·8	3·04	0·99448	7·3	5·86	0·98984
3·9	3·12	0·99434	7·4	5·94	0·98972
4·0	3·20	0·99420	7·5	6·02	0·98960
4·1	3·28	0·99406	7·6	6·11	0·98949
4·2	3·36	0·99392	7·7	6·19	0·98936
4·3	3·44	0·99378	7·8	6·27	0·98924
4·4	3·52	0·99364	7·9	6·35	0·98912
			8·0	6·43	0·98900

The residue in the retort may be used for determining the amount of extractive matter in the beer. For this purpose it is diluted with water, after cooling, till its weight becomes equal to that of the beer before distillation, and the amount of extractive matter is then found from its specific gravity, by means of tables provided for the purpose.

The following is taken from a more detailed table in the *Handwörterbuch*, 2^{te} Aufl. ii. [1] 1081.

TABLE B.—*Specific Gravity and Strength of Malt-Extract.*

Specific Gravity.	Malt-extract in 100 pts. of liquid.	Specific Gravity.	Malt-extract in 100 pts. of liquid.	Specific Gravity.	Malt extract in 100 pts. of liquid.	Specific Gravity.	Malt-extract in 100 pts of liquid.
1·000	0·000	1·018	4·500	1·036	8·925	1·054	13·238
1·001	0·250	1·019	4·750	1·037	9·170	1·055	13·476
1·002	0·500	1·020	5·000	1·038	9·413	1·056	13·714
1·003	0·750	1·021	5·250	1·039	9·657	1·057	13·952
1·004	1·000	1·022	5·500	1·040	9·901	1·058	14·190
1·005	1·250	1·023	5·750	1·041	10·142	1·059	14·428
1·006	1·500	1·024	6·000	1·042	10·381	1·060	14·666
1·007	1·750	1·025	6·244	1·043	10·619	1·061	14·904
1·008	2·000	1·026	6·488	1·044	10·857	1·062	15·139
1·009	2·250	1·027	6·731	1·045	11·095	1·063	15·371
1·010	2·500	1·028	6·975	1·046	11·333	1·064	15·604
1·011	2·750	1·029	7·219	1·047	11·595	1·065	15·837
1·012	3·000	1·030	7·463	1·048	11·809	1·066	16·070
1·013	3·250	1·031	7·706	1·049	12·047	1·067	16·302
1·014	3·500	1·032	7·950	1·050	12·285	1·068	16·534
1·015	3·750	1·033	8·195	1·051	12·523	1·069	16·767
1·016	4·000	1·034	8·438	1·052	12·761	1·070	17·000
1·017	4·250	1·035	8·681	1·053	13·000		

A more extended table of the specific gravity of pure syrup, which does not differ greatly from that of malt-extract, is given in *Ure's Dictionary of Arts, Manufactures, and Mines*, new edition, vol. ii. p. 610.

The amount of alcohol in beer may in most cases be calculated with sufficient accuracy for practical purposes, from the difference between the specific gravity of the boiled and unboiled beer, according to the following principle: *The specific gravity of the unboiled beer is less than that of the boiled beer, in the same proportion as the specific gravity of spirit of wine of equal alcoholic strength is less than that of water.* To determine the amount of alcohol in beer accordingly, the beer is first freed from carbonic acid by brisk agitation in a capacious flask, assisted perhaps by very gentle warming, and its specific gravity is accurately determined. It is then boiled to drive off the alcohol, and the residue is diluted with water, till its weight becomes exactly equal to the original weight of the beer; it is then filtered, if necessary, through a covered filter, and its specific gravity likewise determined. The amount of alcohol is then calculated, as in the following example. Suppose the specific gravity of the unboiled beer, freed from carbonic acid, to be 1·0250; and after boiling and dilution with water, to be increased to 1·0320. Then, according to the principle just stated, the specific gravity of pure spirit of the same alcoholic strength as the beer, will be to that of water as 1·0320 : 1·0250; that is to say, it will be $\frac{1\cdot0250}{1\cdot0320} = 0\cdot9932$, which, according to the table, page 531, corresponds to 3·8 per cent.

The empirical rule for finding the specific gravity of spirit of equal strength with the beer is: *Divide the specific gravity of the unboiled beer by that of the boiled beer, after its original weight has been restored by dilution.*

It is clear that the results obtained by this method (called in Germany the *Specific Beer-test*), will be more exact, in proportion as the composition of the beer differs less from that of pure spirit of equal strength, in other words, the smaller the amount of of the extractive matter contained in the beer. For beers like those of Bavaria, it answers very well; but for those which contain a larger amount of extract it cannot be relied on.

For **Balling's** *Saccharometric method* (*saccharimetrische Bierprobe*), and **Fuchs's** *Hallymetric method* (*hallymetrische Bierprobe*), which latter consists in determining the quantities of alcohol and extractive matter in beer by the quantity of common salt which it is capable of dissolving, see *Handwörterbuch der Chemie*, 2te Aufl. ii. [1] 1078; and *Handbuch der technisch-chemischen Untersuchungen* von P. A. Bolley, 2te Aufl. Leipzig, 1861, s. 350.

The following tables C and D, exhibit the composition of various kinds of beer.—See also *Jahresbericht für Chemie*, 1849, p. 708; 1850, p. 683; 1853, p. 758; 1855, p. 852.

TABLE C.—*Average Amount of Malt-extract and Alcohol in various Kinds of Beer.*

Name of Beer.	Percentage of	
	Malt-extract.	Alcohol.
London Ale, for exportation	7—5	6—8
London Ale, ordinary	5—4	4—5
London Porter, for exportation	7—6	5—6
London Porter, ordinary	5—4	3—4
Brussels Lambik	5·5—3·5	4·5—6
Brussels Faro	5—3	2·5—4
Bière forte de Strasbourg	4—3·5	4—4·5
Bière blanche de Paris	8—5	3·5—4
Bavarian Beer	6·5—4	3—4·5
White Beer of Berlin	6·2—5·7	1·8—2

TABLE D.—*Special Results of the examination of certain Beers.*

Name of Beer.	Percentage of				Analysed by
	Malt-extract.	Alcohol.	Carbonic acid.*	Water.	
London Porter (Barclay and Perkins)	6·0	5·4	0·16	88·44	Kaiser.
London Porter	6·8	6·9	—	86·3	Balling.
London Porter (Berlin)	5·9	4·7	0·37	89·0	Ziurek.
Burton Ale	14·5	5·9	—	79·6	Hoffmann.
Scotch Ale (Edinburgh)	10·9	8·5	0·15	80·45	Kaiser.
Ale (Berlin)	6·3	7·6	0·17	85·93	Ziurek.
Brussels Lambik	3·4	5·5	0·2	90·9	Kaiser.
Brussels Faro	2·9	4·9	0·2	92·0	Kaiser.
Salvatorbier, München	9·4	4·6	0·18	85·85	Kaiser.
Bockbier, München	9·2	4·2	0·17	86·49	Kaiser.
Bavarian Draught beer (*Schenkbier*) München	5·8	3·8	0·14	90·26	Kaiser.
Bavarian Store-beer (*Lager-bier*) München 16 months old	5·0	5·1	0·15	89·75	Kaiser.
Bavarian Store-beer, München	3·9	4·3	0·16	91·64	Kaiser.
Bavarian Draught-beer, Brunswick	5·1	3·5	—	91·1	Otto.
Bavarian Beer, Waldschlösschen	4·8	3·6	—	91·5	Fischer.
Prague Draught-beer	6·9	2·4	—	90·7	Balling.
Prague Town Beer (*Stadt-bier*)	10·9	3·9	—	85·2	Balling.
Sweet Beer, Brunswick	14·0	1·36	—	84·7	Otto.
Josty's Beer, Berlin	2·6	2·6	0·5	94·3	Ziurek.
Werder's Brown Beer, Berlin	3·1	2·3	0·3	94·2	Ziurek.
White Beer, Berlin	5·7	1·9	0·6	91·8	Ziurek.
Bière blanche de Louvain	3·0	4·0	—	93·0	Le Cambre.
Petermann, Louvain	4·0	6·5	—	89·5	Le Cambre.
Mum, Brunswick	45·0	1·9	—	53·1	Freytag and Busse.

The following are examples of the percentage composition of the ash of beer, the first three analysed by Walz (Jahrb. pr. Pharm. iii. 312; Jahresber. f. Chem. 1855, p. 892), the rest by Dickson (Phil. Mag. xxxiii. 341; Jahresber. 1847-8, p. 1112).

TABLE E.—*Ash of Beer.*

	London Beer.	From Monchen.	From Speyer.	Scotch Ale (14 samples).	Scotch Porter (2 samples).	Dublin Porter (2 samples).	London Porter (5 samples).
Potash	38·35	36·58	37·68	3·2—29·8	18·9—20·9	21·4—32·0	4·9 —31·1
Soda	7·68	9·03	6·59	20·9—38·5	33·8—38·8	24·0—42·7	21·8 —50·8
Lime	2·45	1·48	2·98	0·2— 2·0	1·3— 1·6	0·8— 1·5	0·8 — 6·9
Magnesia	3·78	5·64	4·66	0·1— 5·6	0·2— 1·4	0·2— 1·2	0·1 — 1·2
Sulphuric acid (SO^3)	1·36	1·68	2·56	1·6—19·2	2·2— 6·4	2·8—10·1	1·6 —12·2
Chlorine	2·75	3·14	2·11	4·3—18·25	7·4—11·4	6·9—10·1	6·5 —11·5
Silica	9·87	9·96	10·29	4·6—19·1	13·3—18·6	6·9—19·7	8·25—19·7
Phosphoric acid (P^2O^5)	33·76	31·69	33·10	6·0—25·7	12·5—18·8	7·9—20·0	9·3 —20·6
	100·00	100·00	100·00				

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* The blanks in this column indicate that the carbonic acid was not determined quantitatively in the corresponding samples.

Original Gravity of Beer-worts.—The conversion of sugar into alcohol by fermentation, is attended with a diminution of density in the liquid; consequently the specific gravity of beer is always less than that of the wort before fermentation. Now by the revenue-laws of this country, the brewer is allowed a drawback upon all beer that is exported, the amount being regulated according to the original gravity of the wort. Hence it is necessary that the revenue officer be possessed of a method of determining the original gravity, from the observed specific gravity and composition of the beer, whereby he may check the record kept by the brewer.

If the non-volatile matter of beer consisted entirely of starch-sugar (glucose), the determination of the original gravity would be a very easy matter: for it is found that every 1 per cent. of alcohol in beer corresponds very nearly to 2 per cent. of sugar in the wort before fermentation: hence it would merely be necessary to double the percentage of alcohol in the beer, add thereto the percentage of sugar as found by direct experiment, and the sum would be the total amount of sugar in 100 pts. of the unfermented wort; the specific gravity would then be given by a saccharometer-table, such as Table B, p 532.

For example, London porter (No. 1, of Table D), contains 6·0 per cent. of malt-extract (which we shall suppose to consist of starch-sugar), and 5·4 per cent. alcohol, the latter corresponding approximately to 10·8 per cent. starch-sugar. Hence the total quantity of extract in the unfermented wort would be 6·0 + 10·8 = 16·8, giving a specific gravity of 1·06.

But the actual problem to be solved is much less simple: for the wort contains several other substances, all differing more or less in specific gravity from starch-sugar. Hence the exact determination of original gravities can only be effected by special observations. The question has been examined by several foreign chemists, especially by Balling of Prague, in his great work on Brewing[*]; in this country it has been investigated by Messrs. Dobson and Phillips, of the Department of Inland Revenue, and more recently by Professors Graham, Hofmann, and Redwood, from whose "Report on Original Gravities,"[†] the following observations are extracted.

The substances contained in beer-wort, in addition to starch-sugar, are: 1. *Dextrin*, which has not been converted into sugar in the process of mashing. 2. In many instances, *cane-sugar*, the use of which is now permitted in breweries. 3. *Caramel*, arising either from high-dried malt, or from treacle or burnt-sugar, the use of which in the brewery of porter is also allowed by law. 4. A peculiar saccharine substance, called "extractive substance," resembling caramel, possessing decided acid properties, and not fermentable by yeast, even after boiling with sulphuric acid.[‡] 5. Azotised or albuminous matter, derived from the grain. 6. Alkaline and earthy salts.

The albuminous matter and the inorganic salts, have but little effect on the comparative densities of the wort before and after fermentation; but the dextrin, cane-sugar, caramel, and "extractive matter," all give solutions of less specific gravity than a solution of starch-sugar containing the same quantity of carbon, and therefore capable of yielding an equal amount of alcohol. The differences are exhibited in the following table.

TABLE F.—*Specific Gravities of Solutions of various* SACCHARINE SUBSTANCES, *and of* PALE *and* BROWN MALT *containing equal quantities of* CARBON.

Solution of Starch-sugar.	Solution of Cane-sugar.	Solution of Dextrin.	Solution of Extractive Substance.	Solution of Caramel.	Solution of Pale Malt.	Solution of Brown Malt.	Parts of Cane-sugar corresponding in 1000 Parts by Weight of Solution.
1010·4	1010·1	1009·7	1008·9	1008·7	1010·0	1010·0	25
1020·8	1020·2	1019·3	1017·8	1017·3	1020·3	1020·2	50
1031·3	1030·2	1028·8	1026·5	1026·2	1030·6	1030·6	75
1042·4	1040·6	1038·3	1035·5	1034·9	1041·2	1041·2	100
1053·5	1051·0	1047·9	1044·7	1043·8	1052·1	1052·0	125
1064·9	1061·8	1057·3	1053·9	1052·8	1063·0	1062·9	150
1076·0	1072·9	1066·9	1063·0	1062·3	1074·2	1074·0	175
1087·8	1083·8	1067·6	1072·7	1071·8	1085·5	1085·5	200
1099·4	1095·2	1086·3	1082·3	1081·3	1097·2	1097·2	225
1111·4	1106·7	1095·8		1091·0	1109·0	1109·0	250

[*] *Die Gährungschemie wissenschaftlich begründet und in ihrer Anwendung auf die Weinbereitung, Bierbrauerei, Branntweinbrennerei, und Hefenerzeugung praktisch dargestellt.* Von Carl N. Balling. Prague, 1845. Or a shorter treatise by he same author: *Die Saccharometrische Bier- und Branntweinmeischprobe.* Prague, 1846. See also Handwörterbuch d. Chem. 2te Aufl. ii. [1] 1079.

[†] Chem. Soc. Q. J. v. 229.

[‡] It probably contains glycerin and succinic acid, both of which substances have been shown by Pastour to be produced in alcoholic fermentation.

These numbers plainly show that if an unfermented wort contains cane-sugar and dextrin, and the gravity lost by fermentation is inferred from the quantity of alcohol contained in the beer, on the supposition that the fermentable matter consisted wholly of starch-sugar, the estimated gravity will be too high; and on the other hand the conversion of a portion of the fermentable sugar into unfermentable extractive matter, which gives a solution of lower specific gravity for the same amount of carbon, will cause the estimate of the original gravity to come out too low; indeed, the extractive substance indicates only about five-sixths of the saccharine principle from which it is derived.

To obviate these difficulties, the authors of the Report were led to propose,for the determination of original gravities, a purely empirical method, which consisted in fermenting solutions of cane-sugar, starch, sugar, and malt-extract, of known original gravity, and making, at ten or twelve stages of the process, two following observations: 1. Distilling a convenient quantity (4 fluid ounces) of the fermented liquid in a retort as described at page 530, diluting the alcoholic distillate with water, to the original volume of the liquid, and taking its specific gravity; this deducted from the specific gravity of water (= 1000) gives the spirit-indication of the beer: *e.g.* if the specific gravity of the alcoholic distillate after dilution is 985·95, the spirit-indication is 14·05. — 2. Diluting the boiled beer after cooling, to its original volume, taking its specific gravity, and subtracting this, which is called the extract-gravity, from the known original gravity of the wort before fermentation. The difference gives the number of *degrees of gravity lost*, corresponding to the spirit-indication previously observed. The results of a long series of determinations of this kind on liquids of known original gravity are given in the "Report" in the form of tables: of these we shall quote only those which embody the general result of the inquiry, and are intended for actual use in determining the original gravity of beer-worts.

Table G (p. 536) is to be used when the spirit-indication of the beer is found by *distillation* in the manner above-mentioned. The first column gives the integers of spirit-indication, the fractional parts (tenths) thereof being placed at the heads of the other columns; the numbers in these several columns are the degrees of gravity lost corresponding to the several spirit-indications. Thus, suppose that a sample of beer distilled as above, gives a spirit-indication = 9·4, and extract-gravity = 1030·6. On the ninth line of the table, and in the column headed ·4, is found the number 41·2, which is the *gravity lost*, and this added to the extract-gravity, gives 41·2 + 1030·6 = 1071·8 for the original gravity of the wort.

As the distillation of the beer in a retort, and collecting of the entire quantity of alcohol evolved, is an operation which occupies considerable time, and requires some experience in manipulation, it is often desirable to obtain the spirit-indication of the beer by an easier process. This may be done by first taking the specific gravity of the beer deprived of carbonic acid by agitation, then boiling it in a flask till all the alcohol is expelled, diluting it to its original volume, and again taking its specific gravity. The first result, the *beer-gravity*, deducted from the second, the *extract-gravity*, is the new spirit-indication: thus if the beer before boiling has a specific gravity of 1044·7, and after boiling of 1035·1, the spirit-indication is 9·6 degrees. By numerous experiments in which the beer was boiled in a retort, and the alcoholic distillate collected as above, it was found that the second method, the evaporation-method, gives a spirit-indication nearly equal to that resulting from the first or distillation-method, but always sensibly less; thus the spirit-indication of a particular sample was 9·9 degrees by the first method, and 9·6 by the second. The experiments in question were made on liquids of known original gravity, and thus a series of determinations were obtained of the *relation between* the spirit-indication as determined by the *evaporation-method*, and the degrees of gravity lost. The general results of the inquiry, as applied to malt-worts, are given in the Table H, the arrangement of which is the same as that of Table G.

The authors of the Report likewise suggest a rational method of determining original gravities, which is interesting in a scientific point of view, though not expeditious enough for practical use. It is as follows: First determine the amount of alcohol in the beer by distillation. Then treat the residual liquid, which generally contains both starch-sugar and unfermentable extractive matter, with yeast, to complete the fermentation, and determine the additional quantity of alcohol thus produced, making a correction for that which is introduced by the yeast itself. Lastly, make up the remaining spiritless liquor with water to the original volume of the beer, and take its specific gravity, a correction being also made for the increase of gravity caused by the yeast. The quantity of starch-sugar corresponding to the corrected gravity of this solution of extractive matter may now be found from a table provided for the purpose; and this, added to the amount of starch-sugar corresponding to the alcohol, gives the total quantity of starch-sugar, from which the original gravity may be found by the saccharometer tables.

TABLE G. — To be used in ascertaining Original Gravities by the DISTILLATION-PROCESS.

Degrees of Spirit-indication with corresponding Degrees of Gravity lost in Malt-Worts.

Degrees of Spirit-indication.	0	·1	·2	·3	·4	·5	·6	·7	·8	·9
0	—	0·2	0·6	0·9	1·2	1·5	1·8	2·1	2·4	2·7
1	3·0	3·3	3·7	4·1	4·4	4·8	5·1	5·5	5·9	6·2
2	6·6	7·0	7·4	7·8	8·2	8·6	9·0	9·4	9·8	10·2
3	10·7	11·1	11·5	12·0	12·4	12·9	13·3	13·8	14·2	14·7
4	15·1	15·5	16·0	16·4	16·8	17·3	17·7	18·2	18·6	19·1
5	19·5	19·9	28·4	20·9	21·3	21·8	22·2	22·7	23·1	23·6
6	24·1	24·6	25·0	25·5	26·0	26·4	26·0	27·4	27·8	28·3
7	28·8	29·2	29·7	30·2	30·7	31·2	31·7	32·2	32·7	33·2
8	33·7	34·3	34·8	35·4	35·9	36·5	37·0	37·5	38·0	38·6
9	39·1	39·7	40·2	40·7	41·2	41·7	42·2	42·7	43·2	43·7
10	44·2	44·7	45·1	45·6	46·0	46·5	47·0	47·5	48·0	48·5
11	49·0	49·6	50·1	50·6	51·2	51·7	52·2	52·7	53·3	53·8
12	54·3	54·9	55·4	55·9	56·4	56·9	57·4	57·9	58·4	58·9
13	59·4	60·0	60·5	61·1	61·6	62·2	62·7	63·3	63·8	64·3
14	64·8	65·4	65·9	66·5	67·1	67·6	68·2	68·7	69·3	69·9
15	76·5									

TABLE H. — To be used in ascertaining Original Gravities by the EVAPORATION PROCESS.

Degrees of Spirit-indication with corresponding Degrees of Gravity lost in Malt-Worts.

Degrees of Spirit-indication.	0	·1	·2	·3	·4	·5	·6	·7	·8	·9
0	—	0·3	0·7	1·0	1·4	1·7	2·1	2·4	2·8	3·1
1	3·5	3·8	4·2	4·6	5·0	5·4	5·8	6·2	6·6	7·0
2	7·4	7·8	8·2	8·7	9·1	9·5	9·9	10·3	10·7	11·1
3	11·5	11·2	12·4	12·8	13·2	13·6	14·0	14·4	14·8	15·3
4	15·8	16·2	16·6	17·0	17·4	17·9	18·4	18·8	19·3	19·8
5	20·3	20·7	21·2	21·6	22·1	22·5	23·0	23·4	23·9	24·3
6	24·8	25·2	25·6	26·1	26·6	27·0	27·5	28·0	28·5	29·0
7	29·5	30·0	30·4	30·9	31·3	31·8	32·3	32·8	33·3	33·8
8	34·3	34·9	35·5	36·0	36·6	37·1	37·7	38·3	38·8	39·4
9	40·0	40·5	41·0	41·5	42·0	42·5	43·0	43·5	44·0	44·4
10	44·9	45·4	46·0	46·5	47·1	47·6	48·2	48·7	49·3	49·8
11	50·3	50·9	51·4	51·9	52·5	53·0	53·5	54·0	54·5	55·0
12	55·6	56·2	56·7	57·3	57·8	58·3	58·9	59·4	59·9	60·5
13	61·0	61·6	62·1	62·7	63·2	63·8	64·3	64·9	65·4	66·0
14	66·5	67·0	67·6	68·1	68·7	69·2	69·8	70·4	70·9	71·4
15	72·0									

Adulteration of Beer.—The addition of extraneous substances to beer, to give it *colour* and *heading*, or to provide cheaper substitutes for the bitter of the hop, appears to have been formerly carried to a great extent in this country. Dr. Ure says, in his "*Dictionary of Chemistry*" 4th edition, 1831, p. 203: "As long ago as the reign of Queen Anne, brewers were forbid to mix sugar, honey, Guinea pepper, essentia bina, cocculus indicus, or any other unwholesome ingredient, in beer, under a certain penalty; from which we may infer, that such at least was the practice of some; and writers, who profess to discuss the secrets of the trade, mention most of these, and some other articles, as essentially necessary. The essentia bina is sugar boiled down to a dark colour, and empyreumatic flavour. Broom tops, wormwood, and other bitter plants, were formerly used to render beer fit for keeping, before hops were introduced into this country, but are now prohibited to be used in beer made for sale."

"By the present law of this country, nothing is allowed to enter into the composition of beer, except malt and hops. Quassia and wormwood are often fraudulently introduced; both of which are easily discoverable by their nauseous bitter taste. They form a beer which does not preserve so well as hop beer. Sulphate of iron, alum, and salt, are often added by the publicans, under the name of *beer-heading*, to impart a frothing property to beer, when it is poured out of one vessel into another. Molasses and extract of gentian root are added with the same view. Capsicum, grains of paradise, ginger root, coriander seed, and orange peel, are also employed to give pungency and flavour to weak or bad beer. The following is a list of some of the unlawful substances seized at different breweries, and brewers' druggists' laboratories, in London, as copied from the Minutes of a Committee of the House of Commons; *cocculus indicus multum* (an extract of the cocculus), colouring, honey, hartshorn shavings, Spanish juice, orange-powder, ginger, grains of paradise, quassia, liquorice, caraway seeds, copperas, capsicum, mixed drugs. Sulphuric acid is frequently added to *bring beer forward*, or make it hard, giving to new beer instantly the taste of what is eighteen months old."

This appears at first sight, a rather formidable picture of adulteration: nevertheless most of the articles enumerated are perfectly harmless, and of those which are really injurious, the use appears to have very much declined, partly perhaps in consequence of the improved taste of consumers. Formerly there was a preference for what was called *good hard beer*, that is to say beer in which nearly all the sugar and mucilage had been converted into alcohol by fermentation: hence the use of sulphuric acid, as above stated, to simulate the taste of beer thus advanced in fermentation. With regard to burnt sugar or treacle, which is added to porter to give colour and body, its use is now legalised, and therefore it can no longer be regarded as an adulteration.

Picric acid and *cocculus indicus* are sometimes added to give bitterness to beer, especially to bitter ale. The latter of these substances is especially objectionable, as it contains a very poisonous substance, viz. picrotoxin. Picric acid may be detected according to Lassaigne, by treating the liquid, evaporated to half or a quarter of its bulk, with subacetate of lead, or shaking it up with powdered animal charcoal. Pure beer is thereby almost wholly decolorised; but if picric acid is present, the filtered liquid retains a lemon-yellow colour. This reaction is very delicate, sufficing to detect 1 part of picric acid in 12,000 to 18,000 parts of beer. Subacetate of lead likewise precipitates the bitter principle of the hop, and thereby deprives pure beer of its bitterness; but beer containing picric acid remains bitter after being thus treated. According to Pohl (Wien. Akad. Ber. xii. 88), a still more delicate test for picric acid is obtained by immersing unbleached sheep's wool, or any fabric made therewith, in the beer, boiling for six or ten minutes, and then washing the wool. If the beer is pure, the wool remains white, but if picric acid is present, even to the amount of only 1 pt. in 125,000, the wool then appears of a canary-yellow colour, pale or dull according to the quantity.

Picrotoxin may be detected, according to T. J. Herapath, by mixing the beer with excess of acetate of lead; removing the lead from the filtrate by sulphuretted hydrogen; filtering again, boiling for a few minutes; then slowly evaporating the solution till it becomes thickish; shaking it up with pure animal charcoal; collecting the charcoal, which contains the picrotoxin, on a filter; washing it with the smallest possible quantity of water; then drying it at 100° C.; boiling it with alcohol; concentrating the alcoholic filtrate; and leaving it to evaporate. The picrotoxin then separates in well defined quadrilateral prisms; or if the solution be rapidly concentrated, in beautiful feathery tufts. (For figures of these crystals, see *Muspratt's Chemistry*, i. 283.)

Inorganic substances added to beer will be found in the ash. Chalk is sometimes added to sour beer to neutralise the acid; in that case, the ash will contain more lime than the normal quantity. If copperas has been added to promote the *heading*, the liquid will give the reaction of sulphuric acid with chloride of barium, and the ash will contain an abnormal quantity of oxide of iron.

BEGUIN'S VOLATILE SPIRIT, *Spiritus sulphuris Beguini*, consists essentially of sulphide of ammonium with excess of sulphur.

BELLADONNA, OIL OF. An oil expressed in Wurtemberg from the seed of deadly nightshade (*Atropa belladonna*), and used for illumination and for culinary purposes. It is limpid, of golden-yellow colour, of insipid taste, and without odour. Sp. gr. 0·9250 at 5° C. It thickens at −16° C. and solidifies at −25°. The vapours which it exhales during the process of extraction, intoxicate the workmen. The narcotic principle of the plant is retained in the marc, which cannot therefore be used as food for cattle. (Gerh. ii. 881.)

BELLADONNINE. An alkaloïd said to exist in *Atropa belladonna*.

BELL-METAL ORE. See Tin Pyrites.

BELMONTIN. A fatty substance prepared from Burmese naphtha.

BELONITE. Kobell's name for Needle-Ore.

BEN, OIL OF. The oil expressed from the fruits of *Moringa Nux Behen*, Desf.; *Guilandina moringa* Linn.; or *Moringa oleifera* Lam. It is colourless or slightly yellow, of specific gravity 0·912, thick at 15° C., solid in winter. It is odourless, and has a mild taste, is neutral to test-paper, and does not readily become rancid. It is used in perfumery to extract the odorous principle of fragrant plants. In India it is used as an embrocation for rheumatism. According to Völcker (Ann. Ch. Pharm. lxiv. 342), it is saponified perfectly by potash, 400 grammes yielding about 18 grammes of a mixture of solid fatty acids, together with oleic acid. The solid fatty acids are: 1. An acid soluble in strong alcohol, insoluble in ordinary alcohol, melting at 83° C. and containing 81·6 per cent. carbon and 13·8 hydrogen, numbers which approximate to the formula $C^{45}H^{90}O^2$; but the quantity obtained was too small for complete investigation.—2. Ordinary margaric acid.—3. An acid resembling stearic acid, and called by Völcker, *benic acid*.

Another kind of oil of ben, said to be obtained from the seeds of *Moringa aptera*, yields by saponification four fixed fatty acids, viz. stearic acid, margaric acid, and two peculiar acids, *benic acid* and *moringic acid*. (Walter, Compt. rend. xxii. 1143.)

BENIC ACID. This name has been applied to two different fatty acids, mentioned in the last article, both obtained from oil of ben, the one by Völcker, the other by Walter. For distinction, Völcker's acid, which has the higher melting point, may be called *benostearic acid*, and Walter's *benomargaric acid*.

Benomargaric Acid, $C^{15}H^{30}O^2$, crystallises from its alcoholic solution in very bulky nodules, melting at 52° or 53° C.

Benomargarate of ethyl is very soluble in alcohol, and separates from the solution in a crystalline mass. It melts at a very low temperature, even at the heat of the hand. (Walter.)

Benostearic Acid, $C^{21}H^{42}O^2$ according to Völcker, $C^{22}H^{44}O^2$ according to Strecker (Ann. Ch. Pharm. lxiv. 346).—The latter formula agrees with Völcker's analysis better than the former. It is a white crystalline fat, melting at 76° C. and solidifying at 70° C. to a shining white crystalline mass, composed of needles, which may be rubbed to powder; it is soluble in alcohol, and bears a strong resemblance to stearic acid.

Benostearate of sodium, $C^{22}H^{43}NaO^2$, is obtained by saponifying the acid with carbonate of sodium, and dissolving the dried soap in absolute alcohol. The alcoholic solution solidifies after a while to a gelatinous pulp, which is resolved into crystalline grains by drenching it with a large quantity of alcohol. The *barium*-salt, $C^{22}H^{43}BaO^2$, is precipitated on mixing an alcoholic solution of the sodium-salt with chloride of barium. The *lead*-salt, $C^{22}H^{43}BaO^2$, is a white precipitate obtained by mixing the soda soap with acetate of lead.

Benostearate of ethyl, $C^{22}H^{43}O^2.C^2H^5$, is obtained by passing hydrochloric acid gas through a solution of the acid in absolute alcohol. It is a crystalline mass, melting at 48° or 49° C. (Völcker.)

BENZALDIDE. Syn. with hydride of benzoyl. See Benzoyl, Hydride of.

BENZAMIC ACID. Syn. with Oxybenzamic Acid (*q. v.*)

BENZAMIDE. $C^7H^7NO = N.C^7H^5O.H^2$.—*Nitride of Benzoyl* and *Hydrogen*. Liebig and Wöhler, Ann. Ch. Pharm. iii. 268; Fehling, *ibid.* xxviii. 48; Schwarz, *ibid.* lxxv. 195; Laurent, Rev. Scient. xvi. 391; Gerhardt, Traité, iii. lxxv.

This body may be obtained in various ways. 1. By the action of ammonia on bromide, chloride, or cyanide of benzoyl. Chloride of benzoyl, when saturated with perfectly dry ammonia, evolves heat and solidifies into a white mass of benzamide and chloride of ammonium, which must be repeatedly broken up, lest any chloride of benzoyl be enclosed in it, and so escape the action of the ammonia. The sal-ammoniac is extracted with cold water, and the benzamide crystallised from boiling water. Gerhardt prefers pounding chloride of benzoyl in a mortar, with excess of commercial carbonate of ammonium, heating the whole gently, extracting with cold water, and crystallising the residue from alcohol or boiling water. Laurent prepares it by mixing an alcoholic solution of chloride of benzoyl with aqueous ammonia.—2. By the action of ammonia on benzoic anhydride.—3. By the action of ammonia on benzoate of ethyl. The reaction takes place slowly at the ordinary temperature, more rapidly when the ether is heated with aqueous ammonia over 100° C. in a sealed tube (Dumas).—4. By boiling hippuric acid with water and peroxide of lead (Schwarz, Fehling); or by heating it in a stream of dry hydrochloric acid. (Strecker.)

When its hot aqueous solution is cooled suddenly, benzamide separates in small pearly crystals, resembling those of potassic chlorate. When it is cooled slowly, it solidifies into a mass of white shining needles, in which cavities form after a time, containing one or more large crystals; the transformation extends gradually through the whole mass. The finest crystals are obtained from a solution containing a little potash or ammonia. The crystals belong to the trimetric system. Benzamide is inodorous, almost insoluble in cold water, soluble in hot water (especially if it contains ammonia), in alcohol, and in ether. It melts at 115° C., and solidifies on cooling to a crystalline mass; between 286° and 290° it volatilises undecomposed; its vapour smells slightly of bitter almonds, owing to the formation of some benzonitrile, is very inflammable, and burns with a smoky flame.

When vapour of benzamide is passed through a red-hot tube, it is but slightly decomposed, a small portion of a sweetish oil being formed, which, according to Gerhardt, is benzonitrile. It is decomposed at a moderate heat, when passed through a tube filled with pumice-stone, yielding hydrogen, nitrogen, carbonic oxide, and benzol (Barreswil). Benzamide is not decomposed by cold caustic potash; but on boiling, potassic benzoate is formed, and ammonia evolved. It is similarly decomposed by boiling with strong acids, the solution on cooling depositing benzoic acid, while it retains the ammonium-salt of the acid employed. When baryta is heated with benzamide, it undergoes a kind of fusion, and appears to be converted into hydrate of barium; ammonia is evolved, together with the oil which Gerhardt regards as benzonitrile. Benzamide, heated with potassium, yields cyanide of potassium and benzonitrile (cyanide of phenyl), but no ammonia. Heated with benzoic anhydride, or chloride of benzoyl, it yields benzonitrile and benzoic acid:

$$C^7H^7NO + \underset{\text{Benz. anhyd.}}{C^{14}H^{10}O^3} = \underset{\text{Benz. acid.}}{2C^7H^6O^2} + \underset{\text{Benzonitrile.}}{C^7H^5N}$$

$$C^7H^7NO + C^7H^5O.Cl = C^7H^6O^2 + C^7H^5N + HCl$$

Benzonitrile is also formed when benzamide is heated alone, or in a stream of dry hydrochloric acid (Handw.); or treated with phosphoric anhydride or pentachloride of phosphorus. Benzamide is not decomposed by boiling with water and peroxide of lead; but if hydrochloric or sulphuric acid be added, and the whole boiled, filtered, mixed with ammonia, and exposed to the air, it turns brown, and deposits a mould-like substance.

When benzamide is gently heated with fuming hydrochloric acid, it dissolves, combining with the acid, and forming *hydrochlorate of benzamide*, $C^7H^7NO.HCl$, which separates on cooling in long aggregated prisms. It is a very unstable compound; the crystals give off hydrochloric acid when exposed to the air, and in a few days have become opaque, and lost the whole of their acid. (Dessaignes, Ann. Ch. Phys. [3] xxxiv. 146.)

Benzamide is a primary amide, *i. e.* it represents 1 at. NH^3 in which 1H is replaced by benzoyl. The remaining 2H may be wholly or partially replaced by a metal, or an organic acid or basic radicle, secondary or tertiary amides or alkalamides being formed. Those alkalamides which contain organic radicles are described under the corresponding amine; the amides and those of the alkalamides which contain a metal will be described here.

Benzomercuramide. $C^7H^6HgNO = N.C^7H^5O.Hg.H$ (Dessaignes, Gerhardt, *loc. cit.*)—Aqueous benzamide dissolves mercuric oxide abundantly, and the saturated solution solidifies to a crystalline mass, which is coloured with excess of oxide. This is treated with hot alcohol, and the solution on cooling deposits benzomercuramide in white shining laminæ, which may be washed and dried at 100° C. It is readily soluble in alcohol and boiling ether. It is violently attacked by chloride of benozyl, yielding benzoic acid, benzonitrile, and chloride of mercury.

Aqueous benzamide also dissolves small quantities of cupric and argentic oxides; but the compounds have not been examined.

Benzacetosulphophenamide. $C^{15}H^{13}NSO^4 = N.C^7H^5O.C^2H^3O.C^6H^5SO^2$.—Produced by the action of chloride of acetyl on benzosulphophenylargentamide.

Benzocumylsulphophenamide, $C^{23}H^{21}NSO^4 = N.C^7H^5O.C^{10}H^{11}O.C^6H^5SO^2$, is obtained by the action of chloride of cumyl on benzosulphophenargentamide; it crystallises from ether in confused prisms.

Benzosalicylimide. $C^{14}H^9NO^3 = N.C^7H^5O.C^7H^4O''$ (Limpricht, Ann. Ch. Pharm. xcix. 250).—Obtained by heating benzosalicylamic acid (benzosalicylamide) in a small retort to 270° C., until about ⅓ has volatilised, and boiling the residue with small quantities of alcohol, to remove the undecomposed acid. The pulverulent benzosalicylimide is dissolved in a larger quantity of boiling alcohol, whence it separates on cooling in small yellowish needles. It is soluble in about 1000 pts. boiling alcohol.

Benzosulphophenamide. $C^{13}H^{11}NSO^3 = N.C^7H^5O.C^6H^5SO^2.H$ (Gerhardt and Chiozza, Ann. Ch. Phys. [3] xlvi. 145).—Obtained by heating equivalent quantities of chloride of benzoyl and sulphophenamide to 140°—145° C., as long as hydrochloric acid is evolved. The fluid mass crystallises on cooling, and is recrystallised from boiling alcohol. Forms shining, colourless, truncated, interlaced needles, which are slightly soluble in cold water or ether, readily in alcohol. It has a strong acid reaction, and is readily soluble in caustic alkalis. It melts between 135° and 140° C.; when quickly heated, it burns, gives off vapours of benzonitrile, and no longer solidifies on cooling. Its ammoniacal solution becomes syrupy when gently evaporated, and finally solidifies into a radiated mass, which Gerhardt states to be the acid ammonium-salt of *benzosulphophenamic acid*, $C^{26}H^{29}N^3S^2O^8 = NH^3.(C^{13}H^{13}NSO^4)^2$. This salt is very soluble in water and alcohol, but insoluble in ether. When an acid is added to its aqueous solution, an oily substance separates, which soon changes into needles of benzosulphenamide.

Benzosulphophenamide, like many other amides, behaves like a hydrate when acted on by pentachloride of phosphorus, forming the chloride of a peculiar body, which Gerhardt calls *benzosulphophenamidyl.*

$$C^{13}H^{11}NSO^3 + PCl^5 = \underset{\substack{\text{Chloride of benzo-}\\ \text{sulphophenamidyl.}}}{C^{13}H^{10}NSO^2.Cl} + PCl^3O + HCl.$$

The reaction does not take place till heat is applied. The new compound is decomposed by heat into benzonitrile and chloride of sulphophenyl. When it is triturated with carbonate of ammonium it forms an amide, *benzosulphophenamidylamide*, $N.C^{13}H^{10}NSO^2.H^2$, which crystallises from alcohol, and is very slightly soluble in ammonia. (Gerhardt, cited in Handw. ii. [1] 884.)

Benzosulphophenargentamide. $C^{13}H^{10}AgNSO^3 = N.C^7H^5O.C^6H^5SO^2.Ag$.—When nitrate of silver is added to a boiling aqueous solution of benzosulphophenamide containing a little ammonia, there is no precipitate; but on cooling, this compound separates out in colourless needles. It is but slightly soluble in cold water, readily in alcohol. It is decomposed by heat, giving off sulphurous anhydride and benzonitrile, and leaving a residue of metallic silver and carbon. Its solution in strong ammonia yields on evaporation, fine rose-coloured crystals, which contain the elements of 1 at. benzosulphophenamide + 1 at. ammonia. They are readily soluble in boiling water; the solution on boiling deposits crystals of benzosulphophenargentamide; the addition of an acid separates benzosulphophenamide. Gerhardt regards this compound as a diamide, $N^2.C^7H^5O.C^6H^5SO^2.Ag.H^3$, a view which the absence of a diatomic radicle renders improbable.

Benzosulphophenylsodamide. $C^{13}H^{10}NaNSO^3 = N.C^7H^5O.C^6H^5SO^2.Na$.—Benzosulphophenamide dissolves in sodic carbonate with evolution of carbonic anhydride; the solution is evaporated to dryness, and the residue exhausted with boiling alcohol, which deposits the compound on cooling in opaque nodules. It is soluble in water; acids separate from it benzosulphophenamide. (Gerhardt, cited in Handw. ii. [1] 884.)

Dibenzosulphophenamide. $C^{20}H^{15}NSO^4 = N.(C^7H^5O)^2.C^6H^5SO$. (Gerhardt and Chiozza, *loc. cit.*)—Obtained by the action of chloride of benzoyl on benzosulphophenargentamide. Chloride of silver is formed, together with a viscid mass, which dissolves in ether, and crystallises in large brilliant prisms. It melts at 105° C., and is slightly soluble in ammonia. It cannot be obtained by the action of chloride of benzoyl on benzosulphophenamide.

Benzoyl enters into the composition of certain biamides and triamides, forming compounds, which will be described under the original diamides and triamides referred to.

Substitution-products of Benzamide.

Bromobenzamide is not known.—Benzamide dissolves in bromine, without evolution of hydrobromic acid; the solution, after some days, deposits deep-red crystals, having the composition $C^7H^7NOBr^2$, which may be regarded as the hydrobromate of bromobenzamide, $C^7H^6BrNO.HBr$. The crystals are decomposed slowly by water, immediately by ammonia, with separation of benzamide. (Laurent.)

Chlorobenzamide. $C^7H^6ClNO = N.C^7H^4ClO.H^2$ (Limpricht and Uslar, Ann. Ch. Pharm. cii. 263).—Obtained by dissolving chloride of chlorobenzoyl in strong aqueous ammonia; the solution deposits yellow laminæ of chlorobenzamide, which are purified by recrystallisation from hot water or alcohol. It is insoluble in cold water; it fuses at 122° C., and sublimes in small quantities. The compound obtained by Gerhardt and Drion (Ann. Ch. Phys. [3] xlv. 102), by triturating chloride of chlorobenzoyl with carbonate of ammonium, has the same composition with the above, but differs from it slightly in properties, being insoluble in water, soluble in alcohol or ammonia, whence it crystallises in fine needles. It evolves ammonia when boiled with potash.

Nitrobenzamide. $C^7H^6N^2O^3 = N.C^7H^4(NO^2)O.H^2$. (Field, Ann. Ch. Pharm. lxv. 45. Chancel, Compt. Chim. 1849, 180.)—Obtained in small quantity by fusing nitrobenzoate of ammonium. Better, by adding aqueous ammonia to a solution of nitrobenzoic ether in a rather large quantity of alcohol, and allowing the mixture to stand for some days till it is not rendered turbid by water. It is then evaporated on the water-bath till it crystallises on cooling; and the crystals are purified by recrystallisation from mixed alcohol and ether. It is also formed by the action of ammonia on chloride of nitrobenzoyl. Nitrobenzamide is slightly soluble in cold, readily in hot water; also in alcohol, ether, or wood-spirit. From these latter solutions it crystallises in long needles, or, by slow evaporation, in large tables resembling gypsum. It fuses above 100° C., and crystallises on cooling. When boiled with strong potash, it forms potassic nitrobenzoate. Its aqueous solution is decomposed by sulphide of ammonium, as follows:

$$C^7H^6N^2O^3 + 3H^2S = \underset{\substack{\text{Phenyl-}\\\text{carbamide.}\\\text{(Phenyl-urea.)}}}{C^7H^8N^2O} + 2H^2O + S^3$$

Dinitrobenzamide. $C^7H^5N^3O^5 = N.C^7H^3(NO^2)^2O.H^2$ (Voit, Ann. Ch. Pharm. xcix. 105.)—When dinitrobenzoic ether is digested for some days with alcoholic ammonia, it forms a blood-red solution, which deposits dinitrobenzamide in yellowish laminæ and prisms. It has a bitter taste, and dissolves sparingly in cold, more readily in hot water; the solution is neutral. It melts at 183° C., and is decomposed by further heat. Its ammoniacal solution is not precipitated by nitrate of silver.

Thiobenzamide. Schwefelbenzamid. Benzamide sulfuré. $C^7H^7NS = N.C^7H^5S.H^2$ (Cahours, Compt. rend. xxvii. 329).—When a solution of benzonitrile in slightly ammoniacal alcohol is saturated with sulphuretted hydrogen, the liquid becomes brownish-yellow; and if, after some hours, it is boiled down to ¼ its volume, and water added, it deposits yellow flakes, which dissolve in boiling water, and separate on cooling in long yellow silky needles of thiobenzamide. It is decomposed by mercuric oxide, yielding mercuric sulphide, water, and benzonitrile; by potassium, yielding potassic sulphide and cyanide. F. T. C.

BENZAMIL. $C^{28}H^{20}N^2O^2$ (?) (Laurent, Rev. scient. xix. 446.)—Crude bitter-almond oil, shaken up with potash, is distilled till about ⅓ has passed over, the residue dissolved in ether-alcohol, and ammonia passed into the solution. The deposit which forms is separated and boiled with a large quantity of ether; and the solution on cooling deposits silky crystals and a white powder: the latter is benzamil. It is nearly insoluble in alcohol, difficultly soluble in ether. It melts at 170° C., and solidifies very slowly. On dry distillation, it yields a substance soluble in ether. It dissolves in alcoholic potash, and the solution, on cooling, deposits crystals which have not been examined. F. T. C.

BENZANILIDE. Syn. with Phenylbenzamide. See PHENYLAMINE.

BENZENE or **BENZOL.** C^6H^6, or $C^{12}H^6$.—*Benzine, Hydride of phenyl, Bicarburet of hydrogen.* (Faraday, Phil. Trans. 1825, 440. Mitscherlich, Ann. Ch. Pharm. ix. 39. Péligot, Ann. Ch. Phys. [2] lvi. 59. Mansfield, Chem. Soc. Qu. J. i. 244.) —Discovered by Faraday. It is a product of the decomposition of many organic compounds, being formed: 1. When benzoic acid is heated with caustic lime or baryta (Mitscherlich), or when its vapour is passed over red-hot iron (Darcet, Ann. Ch. Phys. [2] lxvi. 99).—2. When phtalic acid is heated with caustic lime (Marignac, Ann Ch. Pharm. xlii. 217), or insolinic acid with baryta (Hofmann). 3. By dry distillation of quinic acid (Wöhler).—4. By passing vapour of bergamot-oil over red-hot lime (Ohme, Ann. Ch. Pharm. xxxi. 318).—5. By passing fats through red-hot tubes (Faraday).—6. By dry distillation of coal (Hofmann, Mansfield).—7. In small quantity, when acetic acid or alcohol is passed through a red-hot tube (Berthelot, Compt. rend. xxxiii. 210). It is also found in Rangoon tar. (De La Rue and Müller.)

The readiest method of preparing pure benzene, is to distil 1 pt. benzoic acid with 3 pts. slaked lime at a gently increasing heat; the mixture of benzene and water which passes over is shaken up with a little potash, the benzene decanted, dried over chloride of calcium, and rectified on the water-bath. 3 pts. benzoic acid yield 1 pt. benzene. The most abundant source of benzene is coal-tar; but the product obtained from this source is very impure, containing several higher hydrocarbons, volatile alkaloids, and other substances. To obtain benzene pure, Mansfield shakes up the light oil obtained by the distillation of coal-tar with dilute sulphuric acid, then with water, and then with potash, in order to remove all the acids and alkaloids that it contains, and submits the washed oil to repeated fractional distillation; the portion which passes over at 80°—90° C. is cooled to −12°, when the benzene crystallises, and is purified from liquid substances by pressure. A better method is to distil the washed light oil in a metal still, and to pass the vapour upwards through a tube surrounded with boiling water, and then into a cooled receiver; thus the oils which boil above 100° C. are condensed and run back into the still. The distillate is similarly treated, the water round the condensing-tube being kept at 80° C. and the distillation stopped when the heat in the retort rises to 90°. This second distillate, (only half of which solidifies at 20°), is shaken up with $\frac{1}{16}$ vol. strong nitric acid, decanted, and shaken up with $\frac{1}{2}$ vol. strong sulphuric acid, rectified without decantation, and the product purified as before by cooling and pressure. Commercial benzene is always very impure, containing many higher hydrocarbons; it may be approximately purified by distillation in the water-bath.

At the ordinary temperature, benzene is a limpid, colourless, strongly refracting oil, of specific gravity 0·85 at 15°·5 C. (Faraday, Mitscherlich), 0·8991 at 0° (Kopp). When cooled, it solidifies into fern-like tufts, or into hard masses like camphor, which melt at 5°·5 C., expanding in bulk at the same time, and solidify again at 0°. At −18°, it is hard, brittle, and of specific gravity 0·956. It boils at 80°·4 at 776 m m. (Kopp), at 86° (Mitscherlich), and volatilises undecomposed. Its vapour-density is (expt.), 2·77 (calc.), 2·704. It has a pleasant smell. It is scarcely soluble in water, but imparts a strong odour to it; readily soluble in alcohol, ether, wood-spirit, and acetone. It dissolves sulphur, phosphorus, and iodine, especially on heating; fixed and volatile oils, camphor, wax, mastic, caoutchouc, and gutta-percha, abundantly; gum-lac, copal, anime, and gamboge, in small quantity; quinine, somewhat readily; strychnine and morphine in small quantity; cinchonine, not at all (Mansfield). Impure benzene is much used to remove stains from silk, &c.

Benzene is very inflammable, and burns with a bright smoky flame. A mixture of 1 vol. benzene with 2 vols. alcohol of 0·85, forms a very good lamp-oil; a larger proportion of benzene gives a smoky flame. When vapour of benzene is passed through a red-hot tube, carbon is separated, and a gaseous hydrocarbon formed. *Chlorine* and *bromine* (not *iodine*), act upon it in the sunshine, forming substitution-products (see below). Strong *nitric acid* converts it into nitrobenzene; according to Abel, the same result is obtained by repeated distillation with dilute acid. *Sulphuric anhydride* or *fuming sulphuric acid* converts it into sulphobenzide and sulphophenylic acid; strong non-fuming sulphuric acid into the latter product only (Gerhardt). According to Mansfield and Mitscherlich, the non-fuming acid has no action upon it. *Potassium, aqueous alkalis*, and *perchloride of phosphorus*, do not act upon benzene, even when heated to its boiling point; neither does aqueous chromic acid (Abel), or phosgene gas in sunshine. (Mitscherlich.)

Church (Phil. Mag. [4] xiii. 415) describes, under the name of *Parabenzene*, a hydrocarbon obtained by him from the light oil of coal-tar, which is isomeric with benzene, but has a different smell, boils at 97°·5 C. and does not solidify at −20°. Nitric acid converts it into nitrobenzene; fuming sulphuric acid into an acid isomeric with sulphophenylic acid, but whose copper- and barium-salts are somewhat different in properties from those of that acid.

Hofmann (Ann. Ch. Pharm. lv. 201) gives a good process for the detection of benzene in a mixture of volatile oils, founded on the facility with which benzene is converted into nitrobenzene by nitric acid, and nitrobenzene into phenylamine by reducing agents. The liquid to be examined is warmed in a test-tube with fuming nitric acid, diluted with water, and shaken up with ether, which dissolves the nitrobenzene. The ethereal solution is separated by a pipette, and mixed with equal volumes of alcohol and hydrochloric acid, and granulated zinc added. After five minutes, the mixture is saturated with potash, again shaken up with ether, which dissolves the liberated phenylamine, and the ethereal solution evaporated on a watch-glass; the addition of a drop of hypochlorite of calcium to the residue gives the intense purple colour characteristic of phenylamine.

Substitution-products of Benzene.

Bromine dissolves in benzene, forming compounds in which 1, 2, and 3 at. H are respectively replaced by Br.

Bromobenzene. Monobromobenzid. Bromide of phenyl, C^6H^5Br (Couper, Ann. Ch. Phys. [3] lii. 309).—The vapour of an equivalent quantity of bromine is passed into a large flask in which some benzene is heated to boiling; the product is washed with potash, dried, and distilled; most of it passes over about 150° C. It is a colourless liquid, smelling like benzene; it does not solidify at − 20° C.; its vapour-density is 5·631. It is not decomposed when heated to 200° C. with acetate of silver, or with a solution of sulphate of silver in strong sulphuric acid. Heated with potassium in a sealed tube, it explodes; with sodium, it yields benzene and a crystalline body. Fuming nitric acid converts it into *bromonitrobenzene*, $C^6H^4BrNO^2$, a crystalline body which melts below 90°, and distils undecomposed. Fuming sulphuric acid dissolves it, forming *bromosulphophenylic acid*.

Dibromobenzene. Bibromobenzid. $C^6H^4Br^2$ (Couper, *loc. cit.*)—When monobromobenzene is acted on for some time by excess of bromine, hydrobromic acid is evolved, and crystals separate, which, by recrystallisation from ether, are obtained in large oblique prisms, which melt at 89° C. and boil at 219° without decomposition.

Tribromobenzene. Terbromobenzid. $C^6H^3Br^3$ (Mitscherlich (1835), Pogg. Ann. xxxv. 374. Lassaigne, Rev. scient. v. 360).—A mixture of benzene and bromine exposed to sunlight gradually forms a solid crystalline body, which is purified by washing with boiling ether. This is the *hydrobromate of tribromobenzene*, $C^6H^6Br^6 = C^6H^3Br^3.3HBr$. It forms a white inodorous tasteless powder, insoluble in water, sparingly soluble in boiling alcohol or ether, whence it crystallises in microscopic oblique rhombic prisms. It is fusible, and crystallises on cooling. When heated, it partly sublimes undecomposed, and is partly resolved into tribromobenzene, hydrobromic acid, bromine, and hydrogen. Heated with hydrate of calcium, it yields *tribromobenzene*. This compound is best obtained by boiling the hydrobromate with alcoholic potash, adding water, dissolving the precipitated oil in ether, and evaporating the solution; it forms silky, very fusible needles, soluble in alcohol and ether, and volatile without decomposition.

Monochlorobenzene. See PHENYL, CHLORIDE OF.

Trichlorobenzene. Chlorobenzid. $C^6H^3Cl^3$ (Mitscherlich, *loc. cit.* Péligot, Ann. Ch. Phys. [2] lvi. 66. Laurent, *ibid.* lxiii. 27).—The action of chlorine in sunshine upon benzene is similar to that of bromine, resulting in the formation of crystals of *hydrochlorate of trichlorobenzene*, $C^6H^6Cl^6 = C^6H^3Cl^3.3HCl$, which are washed with ether or recrystallised from boiling alcohol. It forms colourless shining laminæ, or rhombic prisms with truncated lateral edges, insoluble in water, soluble in alcohol or ether: melts at 132° C. (Mitscherlich); 135°—140° (Laurent); distils completely at 288°, with partial decomposition, without leaving any residue. In its decompositions, it resembles the corresponding bromine compound. *Trichlorobenzene* is obtained by the repeated distillation of the hydrochlorate alone (Mitscherlich): or by heating it with hydrate of barium or calcium, washing the distillate with water, and rectifying it over chloride of calcium; or by boiling it with alcoholic potash (Laurent). It is a colourless oil, of specific gravity 1·457 at 7° C.; boils at 210°; vapour-density 6·37; insoluble in water, soluble in alcohol, ether, or benzene. It is not attacked by chlorine, bromine, acids, or alkalis.

Chlorodinitrobenzene. See CHLORIDE OF DINITROPHENYL, under PHENYL, CHLORIDE OF.

Nitrobenzene. Nitrobenzol. Nitrobenzid. $C^6H^5NO^2$ (Mitscherlich (1834), Pogg. Ann. xxxi. 625).—Formed by the action of fuming nitric acid on benzene, or by the dry distillation of nitrobenzoates. Prepared by gradually adding benzene to warm fuming nitric acid; the nitrobenzene separates as an oil on cooling, is washed with water, and rectified over chloride of calcium. It is a yellowish liquid, with a very sweet taste, and a smell like bitter-almond oil; specific gravity 1·1866 at 14°·4 C. (Kopp); boils at 213° C. (Mitscherlich), 219°—220° (Kopp); vapour-density 4·4. Below 3° C. it crystallises in needles. It is insoluble in water, readily soluble in alcohol and ether. It is much used by perfumers, under the name of *Essence de mirbane*. It is not attacked either by chlorine or bromine at the ordinary temperature; but its vapour is decomposed when passed with chlorine through a red-hot tube, yielding hydrochloric acid. Fuming nitric acid dissolves it, and on heating converts it into dinitrobenzene. Strong sulphuric acid dissolves it, and on heating decomposes it, forming a dark-coloured solution, and evolving sulphurous anhydride. Dilute nitric or sulphuric acid does not attack it, even at 100° C. It is scarcely attacked by boiling with aqueous potash or ammonia, or by distillation over caustic lime; when boiled with alcoholic potash, it yields azoxybenzide (p. 479); and when distilled with alcoholic potash, azobenzide. When a solution of nitrobenzene in alcohol is mixed with ammonia, and saturated with sulphuretted hydrogen, sulphur is deposited, and the product, when cooled to 0° C., solidifies to a mass of yellow needles, which are soluble in water or alcohol and have a biting taste; on driving off the alcohol by heat, more sulphur is deposited, and phenylamine is finally left:

$$C^6H^5NO^2 + 3H^2S = C^6H^7N + 2H^2O + S^3.$$

Other reducing agents, *e.g.* zinc with a mixture of alcohol and hydrochloric acid, iron filings and acetic acid, and arsenite of potassium, convert nitrobenzene into phenylamine.

Dinitrobenzene. $C^6H^4N^2O^4 = C^6H^4(NO^2)^2$ (Deville (1841), Ann. Ch. Phys. [3] iii. 187. Muspratt and Hofmann, Ann. Ch. Pharm. lvii. 214).—Formed very slowly by boiling nitrobenzene with fuming nitric acid; rapidly when nitrobenzene is dropped gradually into a mixture of equal vols. fuming nitric and strong sulphuric acid as long as solution takes place. The mixture is boiled for some minutes, and the crystalline magma which forms on cooling is washed with water and recrystallised from boiling alcohol. It forms long shining needles or laminæ, which melt below 100° C. and solidify into a radiated mass. It is insoluble in water, soluble in warm alcohol. Sulphide of ammonium converts it into nitrophenylamine, and separates sulphur. Zinc and hydrochloric acid convert it into nitrosophenylin (*q. v.*) According to Hilkenkamp (Ann. Ch. Pharm xcv. 86), sulphite of ammonium converts it into a peculiar acid, *dithiobenzolic* or *phenyldisulphodiamic acid*, $C^6H^8N^2S^2O^6$. He obtained this compound by the action of sulphite of ammonium on nitrobenzene, as follows; but he attributes its formation to the presence of dinitrobenzene. He heated 80 grms. nitrobenzene with 240 grms dry sulphite of ammonium, 1 litre absolute alcohol, and some carbonate of ammonium, for 8 or 10 hours on a water-bath. The liquid was filtered from the sulphate of ammonium which separated on cooling, and evaporated to a syrup, when it deposited at first abundance of fine white laminæ, which quickly decomposed, and then a smaller quantity of hard needles, which are the ammonium-salt of this acid.

$$\underset{\text{Dinitrobenzene.}}{C^6H^4N^2O^4} + 6SO^3N^2H^8 = \underset{\substack{\text{Dithiobenzolic}\\ \text{acid.}}}{C^6H^8N^2S^2O^6} + 4SO^4N^2H^8 + 4NH^3.$$

It is readily soluble in water or dilute alcohol, slightly in absolute alcohol, insoluble in ether. Nitric acid colours its solution yellow; chlorine forms with it abundance of chloranil, with traces of a brown resinous substance. The barium-salt is crystalline, soluble in water, insoluble in alcohol. The acid has not been obtained in the free state. F. T. C.

BENZHYDRAMIDE. *Hydride of Cyanazobenzoyl.* $C^{22}H^{18}N^2O$ (Laurent, Ann. Ch. Phys. [2] lxvi. 180; Laurent and Gerhardt, Compt. Chim. 1850, 114).—A product of the action of ammonia on crude bitter-almond oil; or of cyanide of ammonium on hydride of benzoyl.

$$3C^7H^6O + NH^4CN = C^{22}H^{18}N^2O + 2H^2O.$$

Crude bitter-almond oil heated to 100° C., is saturated with dry ammonia, and the product dissolved in ether-alcohol: after twenty-four hours, the solution begins to deposit crystals, which go on increasing for three or four days. The mother-liquor is decanted, and the crystals treated with boiling alcohol, which leaves a white residue, *benzoylazotide*. The solution, on spontaneous evaporation, deposits small needles, mixed with drops of oil: these are washed quickly with a little ether-alcohol, and recrystallised from boiling alcohol. It is also formed in the process for the preparation of azobenzoyl (*q. v.*)

Benzhydramide forms colourless, microscopic, rectangular prisms, with two terminal faces intersecting at an obtuse angle. It is insoluble in water, sparingly soluble in cold alcohol, readily in hot alcohol or in ether. It is very fusible, and solidifies on cooling to a resinous mass, without decomposition: when further heated, it gives off hydrocyanic acid, and yields an oil, a crystalline sublimate, and a little carbon. It is not decomposed by cold dilute hydrochloric acid; but, on boiling, it yields hydride of benzoyl, hydrocyanic acid, and chloride of ammonium. F. T. C.

BENZHYDROCYANIDE. Syn. with Benzimide (*q. v.*)

BENZHYDROL. BENZHYDROLIC ACID. Rochleder and Hlasiwetz gave the name of benzhydrol to a camphor obtained by them from oil of cassia. Further investigation by Rochleder and Schwarz, has shown that this camphor contains two substances, one richer in hydrogen, the other in oxygen: they call the former *benzhydrol*, the latter, *benzhydrolic acid.* F. T. C

BENZIDAM. Syn. with Phenylamine (*q. v.*)

BENZIDINE. $C^{12}H^{12}N^2 = N^2.\overset{\prime\prime}{C^{12}}H^8.H^4$ (Zinin, J. pr. Chem. xxxvi. 93; lvii. 173; Ann. Ch. Pharm. lxxxv. 328.)—An organic alkali formed by the reduction of azobenzene or azoxybenzene. It is obtained by saturating with sulphuretted hydrogen a solution of azobenzene in alcoholic ammonia: the liquid turns brown, and, when heated, deposits sulphur abundantly, which is filtered off. The filtrate, on cooling, deposits crystals of benzidine, which are purified by dissolving them in boiling alcohol, adding dilute sulphuric acid as long as a precipitate forms, washing the precipitate with alcohol, and dissolving it in boiling aqueous ammonia: the solution, on cooling, deposits benzidine in white shining scales. When an alcoholic solution of azobenzene or azoxybenzene is treated with sulphurous acid, sulphate of benzidine is at once precipitated.

Benzidine is inodorous; scarcely soluble in cold water, readily in hot water, alcohol, or ether; its solution has a bitter burning taste. It melts at 108° C., and cools to a crystalline mass: further heated, it partly sublimes, and is partly decomposed. When a solution of benzidine, or its salts, is treated with chlorine, it becomes first blue, then dark brown, and deposits scarlet crystals, scarcely soluble in water, more readily in alcohol (probably azobenzene). Nitrous fumes attack it violently at a gentle heat, and convert it into azobenzene (Noble). It is decomposed by strong nitric acid.

Benzidine combines with acids, forming definite salts, which are mostly readily crystallisable: their solutions are precipitated by caustic alkalis or alkaline carbonates. The *hydrochlorate*, $C^{12}H^{12}N^2.2HCl$, crystallises in white, pearly, rhombic prisms, soluble in water or alcohol, almost insoluble in ether. The *chloroplatinate*, $C^{12}H^{12}N^2.2PtCl^3H$, is a yellow crystalline precipitate, obtained by adding dichloride of platinum to the aqueous or alcoholic solution of the foregoing salt. It is slightly soluble in water, insoluble in alcohol or ether. When boiled with water (more readily with alcohol or ether), it is converted into a dark-violet powder. The *nitrate* forms rectangular prisms, soluble in water. The *acid oxalate*, $C^{12}H^{12}N^2.C^2O^4H^2$, forms white, silky, radiated needles, slightly soluble in water or alcohol. The *acid sulphate*, $C^{12}H^{12}N^2.SO^4H^2$, separates as a dull white powder, when sulphuric acid is added to a solution of benzidine: from a very dilute solution it separates in crystals. It is scarcely soluble in boiling water or alcohol. The *benzoate*, *acetate*, *tartrate*, and *phosphate* are all crystalline. With mercuric chloride, benzidine forms a crystalline double-salt, soluble in water and alcohol. F. T. C.

Diethylbenzidine, $C^{16}H^{20}N^2 = N^2.C^{12}H^{8\prime\prime}.(C^2H^5)^2.H^2$.—The hydriodate of this base, $C^{16}H^{20}N^2.(HI)^2$, or *iodide of diethyl-benzidammonium* $[N^2.(C^{12}H^8)''(C^2H^5)^2.H^4].I^2$, is obtained in crystals by digesting benzidine with alcohol and iodide of ethyl, in a sealed tube at 100° C. for two hours. Treated with ammonia, it yields the free base, which unites with acids forming well crystallised salts. The chloroplatinate, $C^{16}H^{22}Cl^2.2PtCl^2$ is sparingly soluble. (P. W. Hofmann, Proc. Roy. Soc. x. 585; Ann. Ch. Pharm. cxv. 362.)

Tetrethylbenzidine, $C^{20}H^{28}N^2 = N^2.(C^{12}H^8)''.(C^2H^5)^4$, is obtained as a hydriodate by treating the diethylated base with iodide of ethyl. The free base melts at 83° C. resolidifies at 80°, and forms crystalline salts with acids. *Iodide* of ethyl acts but slowly on it, but when treated with *iodide of methyl*, attacks it with energy, forming:

Iodide of Dimethyl-tetrethyl-benzidammonium, $C^{22}H^{34}N^2I^2 = [N^2.(C^{12}H^8)''.(C^2H^5)^4.(CH^3)^2].I^2$. This salt dissolves sparingly in alcohol, but easily in boiling water, whence it crystallises in long beautiful needles. Its solution is not precipitated by ammonia, but yields with oxide of silver, a strongly alkaline solution containing the hydrate $\left.\begin{matrix}N^2(C^{12}H^8)''(C^2H^5)^4(CH^3)^2\\ H^2\end{matrix}\right\}O^2$. This base unites readily with acids, forming beautifully crystalline salts. The *chloroplatinate* $C^{22}H^{34}N^2Cl^2.2PtCl^2$, is almost insoluble in water, but dissolves sparingly in boiling hydrochloric acid, whence it crystallises on cooling in beautiful needles. (P. W. Hofmann, *loc. cit.*)

BENZIL. *Sousoxide de Stilbèse*, $C^{14}H^{10}O^2$. (Laurent. Ann. Ch. Phys. [2] lix. 402. Liebig. Ann. Ch. Pharm. xxv. 25. Zinin, Ann. Ch. Pharm. xxxiv. 190. Gregory, Compt. Chim. 1845. 308.)—Formed by the action of oxidising agents on benzoin. Laurent prepares it by passing chlorine over fused benzoin as long as hydrochloric acid is evolved, and crystallising the product from hot alcohol. Zinin heats gently 1 pt. benzoin with 2 pts. concentrated nitric acid; the reaction is complete when no more nitrous fumes are evolved, and when the yellow oil which rises to the surface is quite clear. This oil solidifies to pure benzil on cooling.

It crystallises by spontaneous evaporation of its alcoholic or ethereal solution in long yellowish six-sided prisms, which are commonly hollow. Observed faces, $\infty P . oP . P$. It is without smell or taste, insoluble in water, soluble in alcohol, ether, and warm sulphuric acid, and reprecipitated from the last by water. It fuses between 90° and 92° C. and solidifies to a fibrous mass: at a higher temperature, it volatilises undecomposed.

It burns with a red sooty flame. It is not altered by boiling with nitric acid or with aqueous potash: but when boiled with alcoholic potash, it turns blue and forms benzilic acid. With ammonia, an alcoholic solution of benzil forms various products, according to the concentration and the duration of the reaction (see AZOBENZIL, BENZILAM, BENZILIM, IMABENZIL). With sulphuretted hydrogen, it deposits sulphur, and forms a yellow oil, smelling of garlic: this oil is more readily obtained by distilling benzil with alcoholic sulphide of ammonium. With sulphide of ammonium, it yields two or three different products, among which is *hydrobenzil* (*q. v.*) Fused with potassium, it gives off violet vapours and leaves a carbonaceous residue.

Benzil is polymeric with the hypothetical radicle benzoyl, C^7H^5O.

Hydrocyanate of Benzil. $C^{16}H^{12}N^2O^2 = C^{14}H^{10}O^2,2HCy$ (Zinin).—When benzil is dissolved in boiling alcohol, and an equal weight of nearly anhydrous prussic acid is added, the mixture gradually deposits white shining rhombic tables of hydrocyanate of benzil. This compound melts and decomposes when heated, leaving pure benzil. It is not attacked when boiled with water or strong hydrochloric acid: when heated with nitric acid or ammonia, it yields benzil. Its alcoholic solution gives with nitrate of silver a precipitate of cyanide of silver, and benzil crystallises from the solution. When its alcoholic solution is heated with mercuric oxide, mercury is reduced, and the smell of benzoic ether becomes distinctly perceptible. F. T. C.

BENZILAM. $C^{14}H^9N$. (Laurent, Rev. scient. xix. 443.)—Formed, together with imabenzil and benzilim, by the action of ammonia on benzil. It is best prepared by dissolving imabenzil or benzilim in sulphuric acid, and adding water, when an oil separates out which speedily solidifies: this is washed with water and a little alcohol, and crystallised from ether-alcohol. It forms colourless rhombic prisms readily soluble in alcohol or ether. It melts at 105° C.: if imperfectly fused, it quickly crystallises on cooling, but if perfectly fused, it solidifies much more slowly, without crystallisation. It is volatile without decomposition. Boiling alcoholic potash has no action upon it: nitric acid decomposes it, yielding an oil which crystallises on cooling, and is insoluble in ether: it is soluble in sulphuric acid, and is reprecipitated by water. F. T. C.

BENZILIC ACID. *Stilbic Acid.* $C^{14}H^{12}O^3$. (Liebig [1838], Ann. Ch. Pharm. xxv. 25. Zinin, *ibid.* xxxi. 329.)—Formed by the action of alkalis on benzil or benzoin. Benzil is dissolved in boiling alcoholic potash, in such quantity that the solution remains distinctly alkaline, and the whole is boiled until a sample of it gives no turbidity when mixed with water. The solution is then evaporated to dryness on the water-bath, the residue powdered, and exposed to an atmosphere of carbonic anhydride till all the potash is converted into carbonate; it is then extracted with alcohol, the solution mixed with water, and, after distilling off the alcohol, decolorised with animal charcoal, and evaporated to crystallisation. The potassic benzilate thus obtained is redissolved in water, and mixed with boiling dilute hydrochloric acid: on cooling, benzilic acid crystallises out.

It forms hard, shining, colourless needles, which are sparingly soluble in cold, more readily in hot water, easily in alcohol or ether. It has no smell, a bitter metallic taste, and a strong acid reaction. It melts at 120° C.; when heated more strongly, it turns red, and emits violet vapours which condense to a brown-red oily liquid, a residue of carbon being left. This oil is volatile, insoluble in water, soluble with a red colour in alcohol or ether: the solution is not decolorised by water, or by hydrochloric or sulphuric acid, but it is decolorised by potash, ammonia, or nitric acid. Benzilic acid burns with a very smoky flame. With strong sulphuric acid all benzilates give a fine crimson colour, which is not easily destroyed by heat disappears on adding water, but reappears on evaporation. It dissolves in warm nitric acid, and is precipitated unchanged by water. Pentachloride of phosphorus converts it into chlorobenzil.

Benzilates.—Their general formula is $C^{14}H^{11}MO^3$. The *lead-salt* is obtained by adding the aqueous acid to neutral acetate of lead. It is a white powder, slightly soluble in hot water: it is unalterable at 100° C., but when strongly heated melts to a red liquid, and emits violet vapours. The *potassium-salt* forms colourless, transparent, anhydrous crystals, readily soluble in water and alcohol, insoluble in ether. It melts at 200 °C., and solidifies on cooling: heated more strongly, it decomposes, yielding a colourless oily distillate, smelling like naphthaline, insoluble in water, soluble in alcohol; the residue contains carbon and potassic carbonate. The *silver-salt* is a white, crystalline powder, obtained by precipitating nitrate of silver by the potassium-salt. It is slightly soluble in hot water; at 100° C. it turns blue, without losing weight, and melts when further heated, emitting violet vapours and leaving metallic silver.

F. T. C.

BENZILIM. *Benzilimide.* $C^{28}H^{22}N^2O^2$ (Laurent [1845], Rev. scient. xix. 442).—One of the products of the action of ammonia on benzil. It is most easily obtained pure by dissolving imabenzil in boiling alcoholic potash, and adding water to the solution. It forms white, silky, very fine needles, sparingly soluble in alcohol or ether. It melts at 130° C. and solidifies slowly in cooling to an amorphous mass. It distils apparently undecomposed, but the distillate is readily soluble in ether, and crystallises from it in needles. It is not attacked by boiling potash or by hydrochloric acid: warm nitric acid attacks it, evolving red fumes, and yielding a yellow oil, which crystallises on cooling, and is insoluble in ammonia, but soluble and crystallisable from ether. It dissolves in warm sulphuric acid, and the addition of water separates benzilam. F. T. C.

BENZIMIC ACID. (Laurent, Compt. Chim. i. 37.)—The name given by Laurent to a peculiar acid which is formed in the preparation of amarine (*q. v.*) It is best prepared by saturating an alcoholic solution of bitter-almond oil with ammonia, letting it stand for 48 hours, and adding water, which takes up benzimate of ammonium. The addition of hydrochloric acid to the aqueous solution precipitates the acid, which is purified by dissolving it in alcohol containing ammonia, boiling the solution, and neutralising with hydrochloric acid. It forms white silky needles, insoluble in water slightly soluble in alcohol: it melts when heated, and cannot be distilled undecomposed. It has not been analysed. F. T. C.

BENZIMIDE. *Benzhydrocyanide. Hydride of Cyanobenzoyl,* $C^{23}H^{18}N^2O^2$. (Laurent (1836), Ann. Ch. Phys. [2] lix. 397: lxvi. 193; Rev. scient. x. 120. Zinin, Ann. Ch. Pharm. xxxiv. 188. Gregory *ibid.* liv. 372. Laurent and Gerhardt, Compt. chim. 1850, 116.)—Formed by the action of hydrocyanic acid on hydride of benzoyl:

$$3C^7H^6O + 2CNH = C^{23}H^{18}N^2O^2 + H^2O.$$

Hydride of benzoyl mixed with ½ its volume of nearly anhydrous prussic acid is shaken up with an equal volume of strong alcoholic potash diluted with 6 pts. alcohol, and the whole gently heated: after a time a white curdy precipitate separates, which is boiled with water, and purified by solution in alcohol. Benzimide also occurs, mixed with hydride of benzoyl and benzoin, in the resinous residue of the rectification of oil of bitter-almonds: it may be extracted by treating the residue with hot alcohol.

Benzimide forms a light loosely-coherent mass, white, with a greenish tinge, and leaves a stain when rubbed or pressed. It is insoluble in water, or in cold potash or hydrochloric acid; sparingly soluble in boiling alcohol or ether. When heated, it melts, and finally volatilises with decomposition, leaving a carbonaceous residue. It dissolves in strong sulphuric acid with a green colour, which soon changes to red, and is reprecipitated by water. Nitric acid dissolves it with decomposition: heated with nitric acid and alcohol, it evolves red fumes and yields ammonia and benzoate of ethyl. Boiled with hydrochloric acid, it yields hydride of benzoyl, sal-ammoniac, and probably also formic acid.

$$C^{23}H^{18}N^2O^2 + 5H^2O = 3C^7H^6O + 2CH^2O^2 + 2NH^3.$$

Heated with strong bases, it yields benzene; and with potassic hydrate moistened with alcohol, it forms ammonia and potassic benzoate. F. T. C.

BENZINE. Syn. with BENZENE (*q. v.*)

BENZOACETIC ANHYDRIDE. See ACETIC ANHYDRIDE.

BENZOANGELIC ANHYDRIDE. See BENZOIC ANHYDRIDE.

BENZOCARBOLIC ACID. BENZOATE OF PHENYL. See BENZOIC ACID.

BENZOCHLORHYDRIN, $C^{10}H^{11}ClO^3$ (Berthelot, Ann. Ch. Phys. [3] xli. 302).—One of Berthelot's artificial fats, containing the elements of benzoic and hydrochloric acids and glycerin, minus water:

$$C^7H^6O^2 + HCl + C^3H^8O^3 = C^{10}H^{11}ClO^3 + 2H^2O.$$

It is prepared by saturating with hydrochloric acid gas a mixture of glycerin and benzoic acid, which is kept for several hours at 100° C., and removing the excess of acid by sodic carbonate: the benzochlorhydrin then sinks to the bottom as an oily liquid. When pure, it is a neutral oil, solidifying at −40°. It is decomposed by potash, yielding potassic chloride and benzoate: and by hydrochloric acid and alcohol, yielding glycerine and benzoate of ethyl. The chlorine is not withdrawn from the compound even by long digestion at 100° with oxide of silver. F. T. C.

BENZOCINNAMIC ANHYDRIDE. See BENZOIC ANHYDRIDE.

BENZOCUMINIC ANHYDRIDE. See BENZOIC ANHYDRIDE.

BENZOCUMYLSULPHOPHENAMIDE. See BENZAMIDE.

BENZOEN. Syn. with Toluol. See BENZYL, HYDRIDE OF.

BENZOERETIC ACID. *Amorphous benzoic acid, Parabenzoic acid* (E. Kopp. Compt. chim. 1849, 154).—An amorphous powder, obtained by heating gum-benzoin with 6 or 8 pts. nitric acid, not strong enough to form nitrobenzoic acid. When quite pure, it is white; but it is commonly yellowish, owing to the presence of a small quantity of a yellow resin, which accompanies it into all its compounds. It is readily soluble in alcohol, ether, and boiling water. It has an aromatic, faintly sour and bitter taste. It melts at 113° C., boils at 256°, and by dry distillation yields pure crystalline benzoic acid, and, if not quite pure, a slight carbonaceous residue. When gently heated, or exposed to the sun, it becomes covered with small crystals of benzoic acid. Distilled with lime, it yields benzene. It forms salts which crystallise with difficulty, and are generally less soluble than the corresponding benzoates. Different specimens have yielded different results to analysis: but in some cases the composition is very near that of benzoic acid. F. T. C.

BENZOGLYCOLLIC ACID. $C^9H^8O^4 = (C^2H^2O)''.C^7H^5O.H.O^2$ (Strecker [1847], Ann. Ch. Pharm. lxviii. 54. Strecker and Socoloff, *ibid.* lxxx. 18. Gössman, *ibid.* xc. 181; xci. 359).—Formed by the action of nitrous anhydride on hippuric acid:

$$2C^9H^9NO^3 + N^2O^3 = 2C^9H^8O^4 + N^4 + H^2O.$$

It is prepared by rubbing hippuric acid to a thin paste with strong nitric acid, and passing a current of nitric oxide into the mixture: nitrogen is then evolved, and the hippuric acid gradually dissolved. After some time, the clear solution becomes opaque from the deposition of benzoglycollic acid: the current of gas is kept up until the liquid assumes a greenish colour, when a large quantity of water is added, and the whole allowed to cool. The acid then separates out in considerable quantities; it is collected on a filter, washed with cold water, suspended in water, neutralised with milk of lime, and the resulting calcium-salt is purified by recrystallisation and pressure between paper, and subsequently decomposed by hydrochloric acid (Socoloff and Strecker). It may also be prepared by slowly passing chlorine into a solution of hippuric acid in excess of moderately dilute potash: when the evolution of nitrogen ceases, the mixture is carefully neutralised by hydrochloric acid, concentrated by gentle evaporation, and mixed with a slight excess of hydrochloric acid, when it solidifies to a crystalline mass. This is purified by solution in ether, and distilling off the ether from the watery layer below it, when the acid separates as an oil in the midst of the water (Gössman). The acid obtained by either of these methods generally contains a large quantity of benzoic acid, which is removed by partially neutralising the acid with milk of lime and evaporating to dryness: benzoic acid, being the weaker acid of the two, remains uncombined, and is extracted from the residue by ether.

Benzoglycollic acid crystallises from alcohol in colourless prisms of 37° 40′ and 142° 20′, which often take the form of thin plates: when precipitated by acids from aqueous solutions of its salts, it separates as a white crystalline powder. It is scarcely soluble in cold, more so in hot water, readily in alcohol and ether: it melts in hot water before dissolving. It melts when heated and solidifies to a crystalline mass; heated more strongly, it gives off vapours containing benzoic acid, and leaves a slight residue of carbon. When boiled for some time with water, it is gradually decomposed into benzoic and glycollic acids:

$$C^9H^8O^4 + H^2O = C^7H^6O^2 + C^2H^4O^3.$$

This decomposition is accelerated by the presence of a mineral acid.

Benzoglycollates are mostly crystalline, soluble in water, some of them in alcohol also. They are neutral to litmus, and have a faint but peculiar taste. Their aqueous solutions may be boiled and even evaporated to dryness without decomposition. From most of their solutions strong acids separate benzoglycollic acid as a crystalline powder. The acid being monobasic, their general formula is $C^9H^7MO^4$.

The *Ammonium-salt* is obtained by saturating the acid with ammonia, or decomposing the calcium-salt with ammonic carbonate. It loses ammonia when evaporated.

The *Barium-salt*, $C^9H^7BaO^4$ + Aq, forms delicate silky needles, which lose their water at 100° C.

The *Calcium-salt*, $C^9H^7CaO^4$ + Aq, forms delicate silky needles, united in groups, which lose their water at 120° C. It dissolves in 42·3 pts. cold, and 7·54 pts. boiling water. It possesses in a remarkable degree the property of forming supersaturated solutions, so that a solution saturated at boiling heat frequently takes some days to deposit all its crystals in successive crops. When a strong solution of this salt is evaporated with chloride of calcium to a syrupy consistence, a double salt separates out on cooling in octahedrons, which are permanent in the air, but are decomposed by water or alcohol into benzoglycollate and chloride of calcium.

The *Copper-salt* crystallises on cooling in abundant blue rhombic tables, when a boiling saturated solution of the calcium-salt is mixed with nitrate of copper. It becomes green and opaque at 100° C, but retains its lustre; is scarcely soluble in cold, more so in hot, water.

The *Ferric salt*, $2Fe^2O^3.3C^{18}H^{14}O^7$ + 28Aq, or $3(\mathit{fe}O.2C^9H^7\mathit{fe}O^4)$ + Aq, is a voluminous flesh-coloured precipitate, insoluble in water, which becomes darker when dried. After drying in the air, it loses 27·36 per cent. (28 at.) water at 100° C.

There appear to be at least two basic *Lead-salts* besides the normal one. When a cold solution of benzoglycollate of calcium is mixed with normal acetate of lead, a flocculent precipitate is formed, which is a mixture of several salts. If this be dissolved in cold water, the solution, on spontaneous evaporation, yields, first, crystals of the salt *b*, and subsequently soft starry crystals of the normal salt $C^9H^7PbO^4$, which melt with partial decomposition at 100° C.

b. $4C^9H^7PbO^4.Pb^2O + 3Aq$, forms hemispherical groups of crystals, which melt at 100°, and lose $1\frac{1}{2}$ at. water.

c. $2C^9H^7PbO^4.5Pb^2O + 2Aq$.—When the cold solution of the calcium-salt is mixed with basic acetate of lead, and the precipitate digested in cold water and filtered, this salt crystallises after some days. It loses 1 at. water at 100° C.

The precipitate obtained by adding the calcium-salt to a boiling solution of normal acetate of lead, is a mixture of several basic salts.

The *Magnesium salt* forms long, very slender needles, readily soluble in water and alcohol.

The *Potassium-* and *Sodium-salts* are obtained like the ammonium-salt. The former crystallises with difficulty, being very soluble. The latter crystallizes more readily from a hot saturated solution in rhombic tables; it contains 3Aq, which it loses at 100° C.

The *Silver-salt*, $C^9H^7AgO^4$, is obtained as a curdy precipitate when the neutral ammonium salt is mixed with nitrate of silver; this precipitate is washed in cold, and dissolved in boiling, water, whence it separates in white microscopic crystals, which when moist quickly blacken in the light; when dry they are not changed at 100° C.

Zinc-salt, $C^9H^7ZnO^4 + 2Aq$. A boiling saturated solution of the calcium-salt mixed with chloride of zinc, yields on cooling long thin needles, which are dried by filter paper and recrystallised. They lose 2 at. water at 100° C. F. T. C.

BENZOHELICIN. $C^{20}H^{20}O^8$. (Piria, Ann. Ch. Phys. [3] xxxiv. 278; xliv. 366.) —The product of the action of the nitric acid on populin. It may be regarded as helicin, ($C^{13}H^{17}O^7$), in which 1 H is replaced by benzoyl, $C^{20}H^{20}O^8 = C^{13}H^{16}(C^7H^5O)O^7$. It is to populin (benzosalicin) as helicin is to salicin.

Obtained by dissolving populin in pure nitric acid of specific gravity 1·3, the solution becomes yellow, and benzohelicin soon crystallises out. On diluting the mother-liquor with water, more crystals separate out. It forms silky needles closely resembling helicin. When boiled with water and magnesia, it is converted into helicin and benzoic acid. Synaptase has no action upon it. Acids and alkalis convert it into benzoic acid, hydride of salicyl, and glucose:

$$C^{20}H^{20}O^8 + 2H^2O = C^7H^6O^2 + \underset{\substack{\text{Hydride}\\\text{salicyl.}}}{C^7H^6O^2} + \underset{\text{Glucose.}}{C^6H^{12}O^6}.$$

F. T. C.

BENZOIC ACID. *Flowers of Benzoin. Hydrate of Benzoyl. Benzoeblumen. Benzoesaüre. Acide benzoïque.* $C^7H^6O^2 = C^7H^5O.H.O.$ [or $C^{14}H^6O^4 = C^{14}H^5O.HO.$]

History and Sources.—First noticed by Blaise de Vigenère (*Traité du feu et du sel*, 1608). Its true composition was determined by Liebig and Wöhler (Ann. Ch. Pharm. iii. 249). It occurs ready formed in gum-benzoin, dragon's blood, storax, Peru and Tolu balsams, and in many other resins and balsams; also in castoreum (Wöhler, Ann. Ch. Pharm. lxvii. 360), in the spindle tree, *Euonymus europæus*, (Schweizer, J. pr. Chem. 411, 437), and in the putrefied urine of man and of graminivorous animals (Liebig, *ibid.* l. 168).

Formation.—It is formed in a great number of organic reactions. 1. By the oxidation of hydride of benzoyl, even by its exposure to moist air. 2. By the action of water on chloride, bromide, or iodide of benzoyl. 3. By heating benzylic alcohol with aqueous chromic acid. 4. By the action of nitric acid on hydride of cinnamyl, cinnamic acid, cinnamol, cumol, and cuminol. 5. By oxidising casein or gelatin with sulphuric acid and binoxide of manganese (Guckelberger, Ann. Ch. Pharm. lxiv. 80). 6. From hippuric acid, by putrefaction, or by boiling with acids or alkalis. 7. By the action of dilute alkalis on populin. 8. By the dry distillation of insolinic (Hofmann) and quinic acids (Wöhler, Ann. Ch. Pharm. li. 145).

Preparation.—Gum-benzoin is employed for the preparation of benzoic acid on the large scale; the process may be conducted either in the dry or wet way. The best method of preparing it in the dry way, or by sublimation, is that given by Mohr, Ann. Ch. Pharm. xxix. 177). The coarsely-powdered resin is placed at the bottom of a round shallow iron-pot, 8 inches in diameter and 2 inches deep; the mouth is closed by a diaphragm of coarse filter-paper, closely cemented to the sides of the vessel; and over this is tied a covering of thick paper, in size and shape like a hat. The vessel is then heated gently and slowly on a sand-bath (1 lb. of gum requires 3 or 4 hours). On removing the paper-cover when the whole is cool, it is found lined with a crystalline sublimate of benzoic acid. The diaphragm allows the vapours of benzoic acid to pass through it, purifies them in great measure from empyreumatic products, and prevents the sublimed acid from falling back into the vessel. About 4 per cent. acid is thus obtained: if the residue in the iron vessel be broken up and again heated, the yield may be increased to 12¼ per cent. The acid prepared by this method, which is on the whole the best for pharmaceutical purposes, is quite pure, with the exception of traces of a volatile oil, which gives it a smell like that of vanilla, and on which its medical properties depend, at least to some extent.—The extraction of the acid from gum-benzoin may be effected more completely in the wet way. Scheele's process (Opusc. ii. 23) is to mix 2 pts. resin with rather less than 1 pt. quick lime, which is first slaked, to digest the mixture for some hours with 20 pts. cold water, and to boil the whole for half an hour. The solution containing benzoate of calcium is filtered from the residue, which is then washed with hot water, evaporated to one-half, and mixed with excess of hydrochloric acid; the benzoic acid which crystallises out on cooling is purified by recrystallisation from hot water, or by sublimation. If sodic carbonate be employed instead of lime, a portion of the resin is apt to be dissolved, which colours the benzoic acid, and cannot be removed without difficulty. Wöhler (Ann. Ch. Pharm. xlix. 245) gives the following method:—Powdered gum-benzoin is dissolved by the aid of heat in an equal volume of alcohol of 90—95 per cent., the hot solution mixed with fuming hydrochloric acid till the residue begins to be precipitated, and the whole distilled as long as its consistency permits; it is then allowed to cool, and again distilled with water as long as any benzoic ether passes over. The joint distillates, containing benzoic ether, alcohol, and hydrochloric acid, are heated with caustic potash until the ether is entirely decomposed, and the resulting solution of potassic benzoate decomposed by hydrochloric acid. The acid thus obtained precisely resembles that prepared by Mohr's method.

Benzoic acid may also be prepared from hippuric acid by boiling it for half an hour with strong hydrochloric acid, and washing the product with cold water. Benzoic acid is sometimes met with in commerce, which is prepared from the urine of graminivorous animals. The urine is allowed to putrefy, then mixed with milk of lime and filtered; and the filtrate is evaporated and precipitated by hydrochloric acid. If the resulting benzoic acid be coloured, it is redissolved in thin milk of lime, the whole boiled with chloride of calcium, hydrochloric acid added, and the precipitate recrystallised from boiling water. The acid thus prepared is inferior to and cheaper than that obtained by sublimation. It always smells of urine, and never has the peculiar smell of the sublimed acid.

Properties.—Benzoic acid crystallises in colourless, transparent, pearly needles or laminæ, which, under the magnifying glass, appear to be six-sided prisms. It has no smell, and a faint but persistent sour and warm taste. It reddens litmus. It melts at 121·4° C. to a colourless liquid of specific gravity 1·0838 (water at 0° being taken as unity), and boils without decomposition at 249·2° (at 740 mm. pressure) (Kopp). It begins to sublime at a much lower temperature, and distils over abundantly with vapour of water. Its vapour-density is 4·27 (Mitscherlich); the vapours excite coughing. It dissolves in 200 pts. cold, and in 24—30 pts. boiling water, much more readily in alcohol and ether. Fats and volatile oils dissolve it abundantly. It dissolves in strong sulphuric acid without decomposition, and is reprecipitated by water. It is not attacked by boiling dilute nitric or chromic acid; and is thus distinguished from cinnamic acid, which, under these circumstances, yields hydride of benzoyl.

Decompositions. 1. *By heat.*—When vapour of benzoic acid is passed through a red-hot tube filled with fragments of pumice-stone, it is decomposed into benzene and carbonic anhydride. The same decomposition takes place at a lower temperature when 1 pt. acid is heated in a retort with 5 or 6 pts. coarsely powdered pumice. If too much heat be applied, naphthalin and some empyreumatic products are also formed, and a residue of carbon left (Barreswil and Boudault). If benzoic acid be heated with lime, only benzene passes over, the carbonic anhydride being retained by the lime. Heated in contact with air, benzoic acid burns with a bright smoky flame, and leaves no residue. 2. Dry *chlorine* acts upon benzoic acid in sunlight, forming a reddish, tough, gummy mass, whence potassic carbonate extracts chlorobenzoic acid (see below), and leaves a brown-red residue, which smells of benzoin, and contains chlorine (Herzog). *Bromine* acts on benzoic acid in similar a manner. When chlorine is passed into a hot aqueous solution of benzoic acid, or when benzoic acid is boiled with aqueous chloride of lime, or with potassic chlorate and hydrochloric acid, a mixture of mono-, di-, and tri-chlorobenzoic acids is obtained; but these acids have not been separated and examined (Stenhouse, Ann. Ch. Pharm. lv. 10). When a solution of benzoic acid in excess of potash is saturated with chlorine, chloroniceic acid, $C^6H^5ClO^2$, is produced (St. Evre). 3. When benzoic acid is heated with strong *nitric acid*, nitrobenzoic acid is formed: a mixture of sulphuric and fuming nitric acid converts it into dinitrobenzoic acid. 4. Fuming *sulphuric acid* converts it into sulphobenzoic acid. 5. Heated to 200° C. with a mixture of anhydrous acid sulphate of sodium, ($Na^2SO^4.SO^3$) and chloride of sodium, it yields chloride of benzoyl together with hydrochloric acid.

$$C^7H^6O^2 + SO^3 + 2NaCl = C^7H^5OCl + HCl + Na^2SO^4.$$

The neutral sulphate of sodium is associated with the sulphuric anhydride to prevent the latter from converting the benzoic acid into sulphobenzoic acid (Beketoff, Ann. Ch. Pharm. cix. 256). 6. *Perchloride of phosphorus* does not act upon benzoic acid till heat is applied, when hydrochloric acid is evolved, and chlorides of benzoyl and of phosphoryl formed. 7. In the animal organism, benzoic acid is converted into hippuric acid, which is found in the urine. (Wöhler, &c.)

Benzoates.—Benzoic acid decomposes carbonates, but an alcoholic solution of potassic benzoate is decomposed by carbonic anhydride, potassic carbonate being precipitated. It is a monobasic acid, but forms some acid and basic salts. The normal benzoates are mostly crystallisable, and soluble in water and alcohol. Their aqueous solutions are decomposed by almost all acids, benzoic acid being precipitated. Alkaline and alkaline-earthy benzoates yield, by dry distillation, benzene, benzone, solid hydrocarbons isomoric with naphthalin, and a metallic carbonate. A mixture of benzoate and formate of potassium yields, when heated, hydride of benzoyl (Piria). With chloride of phosphoryl, alkaline benzoates yield chloride of benzoyl and a phosphate; with chloride of benzoyl, an alkaline chloride and benzoic anhydride. With perchloride of phosphorus or chloride of sulphur, they yield either chloride of benzoyl or benzoic anhydride, according to the proportion of benzoate present.

Benzoate of Ammonium. *a. Normal.*—Obtained in crystals by cooling a solution of benzoic acid in strong warm ammonia; or by evaporating a more dilute solution with addition of ammonia from time to time. It deliquesces in the air, and is soluble in water and alcohol, but less so in the latter than the potassic salt. When heated in a retort, it loses water, and is converted into benzo-nitrile. Its solution loses ammonia on evaporation, yielding:

b. Acid salt.—Obtained in large irregular crystals by the spontaneous evaporation of the solution of *a*. Less soluble than *a* in water and alcohol.

Benzoate of Barium, $C^7H^5BaO^2$ + Aq.—Slender permanent needles (Trommsdorf), or large tables, which become opaque at 100° C. (Plantamour), and lose their water at 110° (Limpricht).

Benzoate of Cadmium, $C^7H^5CdO^2$ + Aq.—By evaporating a solution of carbonate of cadmium in aqueous benzoic acid, shining aggregated needles are obtained, soluble in hot water, sparingly in alcohol. (Schiff.)

Benzoate of Calcium, $C^7H^5CaO^2$ + Aq.—Crystallises in feathery needles or in granules, soluble in 29 pts. cold, and in less hot water.

Benzoate of Copper.—A hot solution of sulphate of copper gives with potassic benzoate an aggregate of bluish-green needles (Ettling), which are anhydrous (Mitscherlich). It dissolves in warm dilute acetic acid, and crystallises thence in small green needles. It is insoluble in alcohol. By dry distillation it yields benzene, benzoic acid, benzoate of phenyl, and an oil which boils at 260° C., and, when heated with sulphuric acid, is decomposed into hydrate of phenyl and a solid hydrocarbon, C^6H^4: the residue contains salicylate of copper.

Ferric Benzoate.—The normal salt crystallises in yellow needles from a solution of ferric hydrate in aqueous benzoic acid; it is soluble with decomposition in water and alcohol, a basic salt being left behind. A still more basic salt is obtained when a solution of ferric chloride, containing enough ammonia to give it a dark-red colour, is mixed with an alkaline benzoate: it is a flesh-coloured precipitate, insoluble in, and not decomposed by, cold water, and containing 17·5 per cent. iron. (Berzelius.)

Ferrous Benzoate crystallises in needles, which effloresce and turn yellow when exposed to the air, and are soluble in water and alcohol. Benzoate of ammonium does not precipitate ferrous salts.

Benzoate of Lead. $C^7H^5PbO^2 + \frac{1}{2}$ Aq.—A light crystalline powder, obtained by precipitating normal lead-salts with potassic benzoate. It melts a little above 100° C., and gives off its water (Berzelius). When digested with basic acetate of lead, it gradually becomes heavy and granular, being converted into a compound of basic benzoate and acetate of lead (Varrentrapp). A basic salt, $C^7H^5PbO^2 \cdot Pb^2O$, is obtained by digesting the normal salt with ammonia, or precipitating benzoate of ammonium with sub-acetate of lead.

Benzoate of Magnesium.—Feathery efflorescent crystals, readily soluble in water.

Manganous Benzoate. $C^7H^5MnO^2 + \frac{1}{2}$ Aq.—Transparent, colourless, permanent needles, soluble in 20 pts. cold, and in a much smaller quantity of boiling water; sparingly soluble in alcohol.

Mercuric Benzoate. $C^7H^5HgO^2 + \frac{1}{2}$ Aq.—A white precipitate, made up of slender needles, obtained by adding an alkaline benzoate to a solution of corrosive sublimate. It is insoluble in cold, tolerably soluble in hot, water; alcohol and ether decompose it, leaving a basic salt, which may also be obtained by boiling benzoic acid with water and excess of mercuric oxide. When treated with ammonia, mercuric benzoate is converted into *ammonio-mercuric benzoate*, a white powder, insoluble in water, almost insoluble in alcohol or ether; potash turns it yellow, and eliminates ammonia: it contains 69·92 per cent. mercuric oxide. (Harff.)

Mercurous Benzoate. $C^7H^5Hg^2O^2$.—A bulky crystalline precipitate, consisting of slender needles; insoluble in cold water; decomposed by boiling water or alcohol, with separation of metallic mercury. Becomes light-yellow when exposed to the light. Treated with ammonia, it is converted into a black powder, containing 80·9 per cent. mercurous oxide.

Benzoate of Potassium. a. Normal. $C^7H^5KO^2$ + Aq.—Crystallises with difficulty from an aqueous solution, more easily from hot alcohol, in feathery needles or pearly laminæ. It is very soluble in water, has a sharp burning taste, and at 100° C. loses its water. Heated with arsenious hydride, it yields benzene. (Darcet.)

b. Acid salt. $C^7H^5KO^2 + C^7H^6O^2$.—Formed in the preparation of acetic anhydride from chloride of benzoyl and acetate of potassium; the residue is washed with water, dried, and dissolved in boiling alcohol, when the acid benzoate crystallises in pearly laminæ. It is slightly soluble in cold water, or in boiling alcohol. (Gregory.)

Benzoate of Silver.—A white curdy precipitate, obtained by double decomposition: it dissolves in a large quantity of boiling water, and crystallises thence in long shining laminæ. When heated, it melts and swells up, and leaves very white metallic silver. It dissolves in 1·96 pts. alcohol, at 100° C. (Mitscherlich.)

Benzoate of Sodium. Efflorescent pointed crystals, soluble in water, sparingly in alcohol.

The *cobalt-*, *nickel-*, and *zinc-salts* are crystallisable and soluble in water and alcohol: the *aluminium-salt*, crystalline, tolerably soluble in water: the *lithium-salt*, uncrystallisable, very soluble: the *bismuth-*, *cerium-*, *tin-*, *yttrium-*, and *zirconium-salts*, are white precipitates, sparingly soluble in water.

BENZOIC ETHERS. *Benzoate of Methyl. Benzoeformester.* $C^8H^8O^2 = C^7H^5(CH^3)O^2$. (Dumas and Peligot [1835]; Ann. Ch. Phys. [2] lviii. 50; Malaguti, *ibid.* [2] lxx. 387.)—Formed, according to Scharling, in the dry distillation of tolu-balsam. For its preparation, 2 pts. benzoic acid, 1 pt. wood-spirit, and 2 pts. strong sulphuric acid, are distilled together, the residue redistilled two or three times with fresh wood-spirit, and the united distillates mixed with water. The impure benzoate of methyl which is thus precipitated, is washed, dried over chloride of calcium, and rectified over oxide of lead, that portion which comes over above 198° C. being collected apart. It may also be prepared by distilling sulphate of methyl with potassic benzoate. It is a colourless, oily liquid, with a pleasant balsamic smell, insoluble in water, soluble in alcohol and ether: boils at 198°·5 C. at 761 mm., or at 199°·2 at 746 mm. (Kopp). Specific gravity 1·10 at 17°, or 1·0876 at 16·3 (Kopp): vapour-density, by experiment, 4·717. Its vapour, passed through a red-hot tube filled with lime, yields, among other products, benzene. It absorbs chlorine without apparent alteration: when the saturated liquid is heated, hydrochloric acid and chloride of methyl pass over first, and then chloride of benzoyl in abundance; the coloured residue contains benzoic acid, benzoate, and (probably) chlorobenzoate of methyl.

Benzoate of Ethyl. Benzoevinester. $C^9H^{10}O^2 = C^7H^5(C^2H^5)O^2$. (Scheele, Opusc. ii. 141; Dumas and Boullay, Ann. Ch. Phys. [2] xxxviii. 20; Wöhler and Liebig, Ann. Ch. Pharm. iii. 274; Deville, Ann. Ch. Phys. [3] iii. 188.)—Benzoate of ethyl is not formed by the mere contact of benzoic acid and alcohol, however prolonged; but the reaction takes place gradually when the mixture is heated to 100° C. in a sealed tube, or when a small quantity of a strong acid is added to it. The statements of Deville and Cahours, that it is formed by the dry distillation of tolu-balsam and gum-benzoin, seem to require confirmation. It is prepared by distilling 4 pts. alcohol with 2 pts. benzoic acid, and 1 pt. fuming hydrochloric acid, till two-thirds have passed over, and pouring back the distillate into the retort two or three times: a little of the ether passes over, but the greater part remains in the residue, whence it is separated by addition of water. Or a solution of 3 pts. benzoic acid in 2 pts. boiling alcohol of 80 per cent. is heated for some time. Liebig and Wöhler prepare it by dissolving chloride of benzoyl in absolute alcohol: heat and hydrochloric acid are evolved, and the addition of water separates the ether. The ether prepared by any of these methods, contains some free benzoic acid, from which it is purified by agitation with sodic carbonate, washing with water, and rectification over oxide of lead.

Benzoate of ethyl is a colourless oil, with a pleasant aromatic smell, and a pungent taste; boils at 212·9° C., when the barometer stands at 745·5 mm. Specific gravity 1·0556 at 10°·5 C. (Kopp). Vapour-density by experiment, 5·406. It is slightly soluble in water, soluble in all proportions in alcohol and ether. It burns with a bright smoky flame. Chlorine does not act upon it below 60° or 70° C., when hydrochloric acid and chloride of ethyl pass over: on heating the mixture, a colourless distillate passes over at 190°, to which Malaguti (Ann. Ch. Phys. [2] lxx. 374), assigns the formula $C^{18}H^{16}Cl^{6}O^{3}$, regarding it as a compound of chloride of benzoyl with bichlorovinic ether: the black residue, when further heated, yields chloride of benzoyl. Nitric acid, or a mixture of nitric and sulphuric acids, converts it into nitrobenzoate of ethyl. It is not attacked by perchloride of phosphorus (Cahours). When distilled over fused chloride of zinc, it yields chloride of ethyl and benzoate of zinc, which latter is decomposed by further heat, forming benzoic acid and benzene. Ammonia acts upon it slowly, at the ordinary temperature; but, if the mixture be heated above 100° C. in a sealed tube, benzamide is readily formed. Aqueous potash converts it very slowly into alcohol and potassic benzoate: when heated with solid potash or potash-lime, hydrogen is evolved, and benzoate and acetate of potassium formed (Dumas and Stas). Sodium acts upon it between 60° and 70° C.: the liquid turns brown, without evolution of gas, yielding, among other products, the ether of a peculiar acid. (See HYPOBENZOYLOUS ACID.)

Benzoate of Ethylene. Benzoate of Glycol. $C^{16}H^{14}O^{4} = (C^{7}H^{5}O)^{2}.(C^{2}H^{4})''.O^{2}$. (M. Simpson and Wurtz, Ann. Ch. Phys. [3] lv. 400.)—Obtained by the action of dibromid of ethylene on benzoate of silver. It is soluble in ether, and crystallises from the solution in colourless, shining, right-rhombic prisms. Melts at 67° C., and distils without alteration at a temperature above the boiling point of mercury.

Benzoate of Amyl. $C^{12}H^{16}O^{2} = C^{7}H^{5}(C^{5}H^{11})O^{2}$ (Rieckher, (1847), Jahr. pr. Pharm. xiv. 15).—Obtained by distilling 1 pt. fusel-oil and 2 pts. sulphuric acid with excess of alkaline benzoate. It is a yellowish oil of peculiar smell: boils at 260·7° C. when the barometer stands at 745·6 mm. Specific gravity 0·9925 at 14°·4 (Kopp): readily decomposed by alcoholic potash.

Benzoate of Allyl. Benzoepropylenyl. $C^{10}H^{10}O^{2} = C^{7}H^{5}(C^{3}H^{5})O^{2}$ (Zinin, Ann. Ch. Pharm. xcvi. 362; Cahours and Hofmann, *ibid.* cii. 297; Berthelot and De Luca, Ann. Ch. Phys. [3] xlviii. 286).—Obtained by distilling equal quantities of iodide of allyl and benzoate of silver, washing the distillate with sodic carbonate, and rectifying over oxide of lead. Also by the action of chloride of benzoyl on allylic alcohol. A yellow aromatic oil, heavier than water: boils at 230°—240° C.: insoluble in water, soluble in alcohol or ether: decomposed by boiling with potash.

Benzoate of Benzyl. Benzoate of Tolyl. (Canizzaro.) $C^{14}H^{12}O^{2} = C^{7}H^{5}(C^{7}H^{7})O^{2}$. —When chloride of benzoyl and benzylic alcohol are distilled together in equal proportions, hydrochloric acid is evolved, benzoic acid and chloride of benzyl pass over, and finally benzoate of benzyl, in the form of a yellowish oil, which crystallises on cooling. It is purified by pressure between filter-paper, rectification over benzoic anhydride, washing with sodic carbonate, and another rectification. It forms colourless crystalline laminæ, which melt below 20° C., and boil at about 345°. After fusion, it recrystallises with great difficulty, often requiring the aid of a freezing mixture. It is isomeric with benzoin.

Benzoate of Glycyl. See BENZOICIN.

Benzoate of Phenyl. Benzophenid. Benzoeoxyd. Benzocarbolic acid. $C^{13}H^{10}O^{2} = C^{7}H^{5}(C^{6}H^{5})O^{2}$. (Ettling (1845), Ann. Ch. Pharm. liii. 87; Stenhouse, *ibid.* liii. 91; Laurent and Gerhardt, *ibid.* lxxv. 75; List and Limpricht, *ibid.* xc. 190.) —Obtained by the action of chloride of benzoyl on phenylic alcohol or phenylate of potassium: by the dry distillation of benzoate of copper (Ettling): by heating benzosalicylic anhydride (Gerhardt). List and Limpricht have shown the identity of the substances obtained by all these methods. It is best prepared by heating phenylic alcohol with chloride of benzoyl, as long as hydrochloric acid is evolved, washing the crystalline product with potash, exhausting it with ether-alcohol, and evaporating the solution to crystallisation. To obtain it from benzoate of copper, the dry salt is distilled over the open fire as long as vapours are evolved; the distillate again distilled with excess of sodic carbonate, as long as benzene passes over with aqueous vapour; the insoluble residue in the retort separated from the alkaline liquid, washed with water, and dissolved in hot alcohol; and the crystals which separate on cooling, purified by repeated crystallisation from hot alcohol. (List and Limpricht.)

Benzoate of phenyl forms hard, shining, colourless, rhombic prisms, often half an inch long. It melts at 66° C., and cools to a crystalline mass: at a higher temperature it volatilises undecomposed. It has a faint smell of geraniums, or, when heated, of lemons: is insoluble in water, soluble in alcohol and ether, especially on heating. It burns with a red, very smoky flame. Chlorine and bromine convert it into substitution-products (see below). Sulphuric acid dissolves it readily; the addition of water separates benzoic acid, while sulphophenylic acid remains in solution. Boiling hydrochloric acid does not attack it. It is not decomposed by boiling with aqueous potash, but, if the mixture be heated to 150°—170° C. in a sealed tube, potassic benzoate and phenylate are formed: the same decomposition is effected by fusion with solid potash, or by contact with alcoholic potash, even in the cold. It may be boiled with alcoholic ammonia without decomposition; if the mixture be heated to 150° C. in a sealed tube, phenylic alcohol and benzamide are formed, but no aniline. It is similarly decomposed when distilled in a stream of dry ammonia. Perchloride of phosphorus does not attack it. (List and Limpricht.)

Substitution-products of Benzoate of Phenyl.

1, 2, or 3 at. H in benzoate of phenyl may be replaced by Br, Cl, or NO^2. These substitution-products are obtained either by the direct action of chlorine, bromine, or nitrosulphuric acid, on benzoate of phenyl; or by the action of chloride of benzoyl on the substitution-products of hydrate of phenyl.

Benzoate of Bromophenyl, $C^{13}H^9BrO^2 = C^7H^5(C^6H^4Br)O^2$, and of *Dibromophenyl*, $C^{13}H^8Br^2O^2 = C^7H^5(C^6H^3Br^2)O^2$. *Bromo-* and *Dibromo-benzophenid.* (List and Limpricht, *loc. cit.*)—When dry benzoate of phenyl is treated with bromine as long as any hydrobromic acid is evolved, the excess of bromine distilled off, and the residue repeatedly crystallised from hot alcohol, large colourless needles are obtained, which melt below 100° C., sublime undecomposed, and are insoluble in water, but soluble in hot alcohol and ether. From the great variation in the analyses, this compound is certainly a mixture of at least two substitution-compounds: and it is probable that tribromobenzophenide is present also. The substance is dissolved and decomposed by cold alcoholic potash, into benzoic, bromophenylic, and dibromophenylic acids.

Benzoate of Chlorophenyl. Chlorobenzophenid. $C^{13}H^9ClO^2 = C^7H^5(C^6H^4Cl)O^2$. (Stenhouse, *loc. cit.*)—When dry chlorine is led for some days over fused benzoate of phenyl, a dark-yellow mixture is produced, consisting of an oily and a solid body, having a very pungent smell: this is pressed between filter-paper, and the solid residue repeatedly crystallised from ether. Large flat crystals are thus obtained, which melt at 84° C., and sublime in four-sided prisms: they have a faint smell, like that of sesquichloride of carbon. From analyses, this substance appears to be a mixture of chloro- with dichloro-benzophenide. The oily substance contains more chlorine, and probably consists in part of trichlorobenzophenide. Both compounds, when heated with alcoholic potash, yield chloride and benzoate of potassium, and on addition of hydrochloric acid, a dark, resinous body, smelling of creosote, which is probably impure chlorophenylic acid.

Benzoate of Dinitrophenyl. Dinitrobenzophenide. $C^{13}H^8N^2O^6 = C^7H^5(C^6H^3(NO^2)^2)O^2$. (Laurent and Gerhardt, *loc. cit.*)—Dinitrophenylic acid is heated with chloride of benzoyl, as long as hydrochloric acid is evolved; and the product is extracted with dilute ammonia, washed with cold alcohol, and crystallised from boiling alcohol. Yellow rhombic laminæ, insoluble in water, slightly soluble in hot alcohol, more readily in warm ether, partly soluble in potash.

Benzoate of Trinitrophenyl. Trinitrobenzophenide. $C^{13}H^7N^3O^8 = C^7H^5(C^6H^2(NO^2)^3)O^2$.—Prepared like the preceding compound, trinitrophenylic (picric) acid being substituted for dinitrophenylic acid. Shining yellow rhombic laminæ, less soluble in all menstrua than the dinitro-compound. When heated, it melts and solidifies to a crystalline mass: heated more strongly, it explodes. Dissolves in boiling potash, forming a dark-red solution, whence acids precipitate crystalline flakes.

Substitution-products of Benzoic Acid.

BROMOBENZOIC ACID. $C^7H^5BrO^2$. (Péligot [1836], Ann. Ch. Pharm. xxviii. 246; Herzog, N. Br. Arch. xxiii. 16; Müller, Compt. rend. xxx. 325.)—Benzoic acid is treated with bromine in the sunshine, the excess of bromine distilled off, the residue dissolved in sodic carbonate (when an oil containing bromine remains undissolved), and the solution precipitated by nitric acid (Herzog). Péligot makes bromine-vapour act upon benzoate of silver, by placing the salt, together with a tube containing bromine, in a closed vessel, and leaving it for twenty-four hours: from the product the bromobenzoic acid is dissolved out by ether. The solution, on evaporation, yields a brown oil, which crystallises on cooling: this is dissolved in potash, treated with animal charcoal, and reprecipitated by nitric acid. It forms a colourless crystalline mass, which melts at 100° C., and sublimes at 250°, leaving a residue of carbon. It burns with a smoky green-edged flame: is sparingly soluble in water, readily in alcohol and ether.

Bromobenzoates are generally soluble and crystallisable: the *lead-*, *copper-*, and *mercurous-salts* are less soluble. The *silver-salt*, $C^7H^4AgBrO^2$, is soluble in warm water.

CHLOROBENZOIC ACID. *Chloromichmylic acid.* $C^7H^5ClO^2$. (Herzog, 1840, N. Br. Arch. xxiii. 15; Scharling, Ann. Ch. Pharm. xli. 49; xlii. 268; Stenhouse, *ibid.* lv. 1; Field, *ibid.* lxv. 55; Limpricht and v. Uslar, *ibid.* cii. 259; Chiozza, Ann. Ch. Phys. [3] xxxvi. 102).—When dry benzoic acid is acted on by chlorine, a moist viscid reddish mass is formed, which appears to contain a mixture of mono-, bi-, and trichlorobenzoic acids; these acids (which Stenhouse also obtained by treating benzoic acid with chloride of lime and hydrochloric acid), cannot be separated from each other. Limpricht and Uslar obtained pure chlorobenzoic acid from chloride of chlorobenzoyl. According to them, the acid obtained by Chiozza, by the action of perchloride of phosphorus on salicylic acid, is not identical, but isomeric, with chlorobenzoic acid: we shall describe it separately as *parachlorobenzoic acid.* There is no doubt that the chloromichmylic acid obtained by Scharling by distilling urine with nitric acid, is identical with chlorobenzoic acid.

Limpricht and Uslar boil chloride of chlorobenzoyl (obtained by the action of perchloride of phosphorus on chlorosulphobenzoic acid) with potash, and saturate the solution with hydrochloric acid: the precipitated chlorobenzoic acid is purified by recombination with a base and reprecipitation by an acid. It forms colourless, concentrically-grouped prisms, which melt at about 140° C., but sublime at a lower temperature in small needles. It dissolves sparingly in cold water, readily in hot water, alcohol, or ether. Fuming nitric acid converts it into nitrochlorobenzoic acid. The *chlorobenzoates* are generally soluble. The solution of the *ammonium-salt* gives off ammonia abundantly when evaporated, so that the residue is nearly pure chlorobenzoic acid. The acid which Field obtained by boiling benzoic acid with potassic chlorate and hydrochloric acid, melts with difficulty, and blackens when heated. The *barium-* and *calcium-salts* crystallise with 1½ aq., which they lose at 100° C. The *lead-salt* is a white precipitate, which melts and turns yellow at 110°. The *potassium-* and *sodium-salts* are uncrystallisable. The *silver-salt*, $C^7H^4AgClO^2$, is a white precipitate, consisting of microscopic needles. *Chlorobenzoic ether* (chlorobenzoate of ethyl), $C^9H^9ClO^2 = C^7H^4(C^2H^5)ClO^2$, is obtained by treating the acid with alcohol and sulphuric acid, or chloride of chlorobenzoyl with alcohol, and precipitating the product with water. It is a liquid smelling like benzoate of ethyl, and boiling at 245° C. It dissolves in nitrosulphuric acid, and water precipitates from the solution an oil which gradually solidifies into crystals, probably of *nitrochlorobenzoic ether.*

Parachlorobenzoic Acid, $C^7H^5ClO^2$ (Chiozza, *loc. cit.*)—Salicylic acid is distilled with perchloride of phosphorus, and the distillate rectified, when a heavy, strongly refracting oil passes over between 200° and 250° C., which is converted gradually by cold, immediately by hot water, into hydrochloric and parachlorobenzoic acids: the oil is probably the chloride corresponding to the acid. Parachlorobenzoic acid forms colourless shining crystals, like those of salicylic acid, from which it is distinguished by giving no violet colour with ferric salts. It melts at 130° C., and sublimes undecomposed: dissolves readily in hot water, and the saturated solution solidifies on cooling into a mass of needles. Some of its salts differ from the corresponding chlorobenzoates in the amount of water of crystallisation which they contain: thus the *barium-salt* is anhydrous, and the *calcium-salt* contains 1 aq. The *silver-salt* may be obtained in rather large crystals.

NITROBENZOIC ACID, $C^7H^5NO^4 = C^7H^4(NO^2)O^2$. (Plantamour [1839], Ann. Ch. Pharm. xxx. 349; Mulder, *ibid.* xxxiv. 297; Abel, *ibid.* lxiii. 313; Bertagnini, *ibid.* lxxix. 259; Blumenau, *ibid.* lxxxvii. 127; Gerland, *ibid.* xci. 185). Mulder's method of heating benzoic acid with fuming nitric acid, is a long process. Gerland recommends agitating 1 pt. benzoic acid and 2 pts. nitre with strong sulphuric acid, and heating the whole till it softens: the resulting nitrobenzoic acid is purified by crystallisation from boiling water. The acid is also formed by the decomposition of several organic compounds: by the oxidation of hydride of nitrobenzoyl by chromic acid (Bertagnini): by boiling cinnamic acid and other cinnamyl-compounds (Plantamour, Mulder), cumene (Abel), or dragon's blood (Blumenau), with nitric acid: by heating nitrohippuric acid with hydrochloric acid (Bertagnini). Nitrobenzoic acid forms colourless laminæ, generally grouped together. It melts at 127° C., but sublimes at 110°, and if pure, leaves no residue: the vapours excite coughing. When boiled it blackens and decomposes. It dissolves in 400 pts. water, at 10°, and in 10 pts. at 100°, forming strongly acid solutions; it melts in water below 100°, to a heavy oil: is readily soluble in alcohol and ether. Strong nitric or hydrochloric acid dissolves it without decomposition: but it is decomposed by prolonged boiling with nitric acid. It dissolves in cold sulphuric acid: on heating the solution, some nitrobenzoic acid sublimes, and near the boiling point of sulphuric acid the mixture becomes red, a peculiar compound being formed (Mulder). It is not altered by sublimation in dry chlorine. Perchloride of phosphorus attacks it when heated, yielding chlorides of nitrobenzoyl and of phosphoryl. With sulphide of ammonium it forms benzamic acid (*q. v.*) In the animal system it is converted into nitrohippuric acid, which appears in the urine.

Nitrobenzoates are generally crystallisable and soluble in water and alcohol: they explode when heated, and give off nitrobenzol. Nitrobenzoic acid is a strong acid, and decomposes the salts of many other acids. The normal *ammonium-salt* loses ammonia when heated, and yields an acid salt, which also crystallises when the solution of the normal salt is evaporated: the normal salt on prolonged fusion, yields nitrobenzamide (Field). The *barium-salt*. $C^7H^4BaNO^4$ + 2aq., forms fine crystals which lose their water at 100° C. The *calcium-salt* contains 1 aq., which it loses at 130°—180° C. The *copper-salt* is a blue powder, which separates on cooling from a hot mixture of the acid with cupric acetate: at 130° C. it loses water and some acid. The *ferric salt* is anhydrous: it is obtained as a bulky flesh-coloured powder, when a boiling solution of the acid is precipitated by ferric chloride. The normal *lead-salt* is obtained in crystals when a boiling solution of the acid is added to basic acetate of lead, until a permanent precipitate is formed: it is decomposed by washing with water, and yields basic salts.

The *manganese-salt* contains 2 aq., one of which it loses below 100°, the other at 133° C. The *potassium-* and *sodium-salts* crystallise with difficulty: when heated, they are decomposed, emitting sparks. The *silver-salt*, $C^7H^4AgNO^4$, is obtained in pearly laminæ, by crystallising from hot water the precipitate which nitrobenzoate of ammonium gives with nitrate of silver: at 120° C. it turns grey, and loses acid, at 250° it explodes in closed vessels, forming nitrobenzenel. The *zinc-salt* contains 2½ aq., which it loses at 140°: it crystallises from the filtrate which runs off from the gelatinous precipitate formed by nitrobenzoate of ammonium with sulphate of zinc: this precipitate is a basic salt.

Nitrobenzoic Ethers. Nitrobenzoate of Methyl, $C^8H^7NO^4 = C^7H^4(CH^3)(NO^2)O$ (Chancel, Compt. Chim. 1849, 179; Bertagnini, Ann. Ch. Pharm. lxxix. 269.) — Prepared in a similar manner to nitrobenzoate of ethyl, which it resembles in all its reactions. It forms small, white, nearly opaque right rhombic prisms, which melt at 70° and boil at 129° C.: are insoluble in water, slightly soluble in alcohol and ether, somewhat more in wood-spirit: have a faint aromatic smell, and a cooling taste.

Nitrobenzoate of Ethyl. $C^9H^9NO^4 = C^7H^4(C^2H^5)(NO^2)O^2$. (E. Kopp, Compt. rend. xxxiv. 615; Chancel, *loc. cit.*; Bertagnini, *loc. cit.*; List and Limpricht, Ann. Ch. Pharm. xc. 206.)—A boiling alcoholic solution of nitrobenzoic acid is saturated with hydrochloric acid: after some time water is added, and the precipitated ether is agitated with hot sodic carbonate, washed with cold water, dried between filter-paper, and crystallised from ether-alcohol. Bertagnini prepares it by crystallising a solution of chloride of nitrobenzoyl in alcohol; and List and Limpricht, by dropping benzoate of ethyl into a mixture of 1 pt. nitric and 2 pts. sulphuric acid. It forms right rhombic prisms, which melt at 42°, and boil at 298° C.: smells like strawberries, and has a fresh taste; is insoluble in water, readily soluble in alcohol and ether. Boiling potash decomposes it into alcohol and nitrobenzoic acid: with ammonia it forms nitrobenzamide and alcohol: with sulphide of ammonium, benzamate of ethyl.

Nitrobenzoate of Dibromophenyl. (*Nitrobibromobenzophenide.*) $C^{13}H^7BrNO^4 = C^7H^4(C^6H^3Br^2)(NO^2)O^2$ (List and Limpricht, *loc. cit.*)—Separates as a resin when benzoate of dibromophenyl is added to nitrosulphuric acid; the addition of water scarcely precipitates anything more. It crystallises from hot alcohol in nodules, composed of small needles: from a concentrated solution, it separates as an oil. It melts between 90° and 100° C.: is insoluble in water, sparingly soluble in hot alcohol. Alcoholic potash decomposes it into nitrobenzoic and dibromophenylic acids.

Nitrobenzoate of Dinitrophenyl. $C^{13}H^7N^3O^8 = C^7H^4[C^6H^3(NO^2)^2](NO^2)O^2$ (List and Limpricht, *loc. cit.*)—Powdered benzoate of phenyl is added to cold nitrosulphuric acid, whereupon it dissolves, and yellow crystals separate out, which are increased by the addition of water; these are washed, first with cold water, then with alcohol. It forms a white crystalline powder, which turns yellow when heated, and melts at 150° C.: on cooling, it solidifies to a yellow glass, which gradually becomes opaque. It is insoluble in cold water or alcohol, sparingly soluble in hot alcohol or in ether. Heated on platinum-foil, it burns with yellow smoky flame: heated in a tube, it explodes feebly. It is decomposed by alcoholic potash. Sulphide of ammonium dissolves it with deep-red colour: by evaporation on a water-bath, a dark-violet resinous mass is obtained partly soluble in acids.

Dinitrobenzoic Acid. $C^7H^4N^2O^6 = C^7H^4(NO^2)^2O^2$ (Cahours, Ann. Ch. Phys. [3] xxv. 30).—When fused benzoic acid is gradually added to a warm mixture of nitric and sulphuric acids, it dissolves with slight evolution of gas: the whole is then boiled (for 1 hour, Cahours;—for 6 hours, Voit), and as soon as it begins to be turbid, it is cooled and water added, which precipitates yellow flakes, which are washed with water, dried, and crystallised from boiling alcohol. Dinitrobenzoic acid is thus obtained in short shining prisms, which melt at a gentle heat, and sublime in delicate needles. It is slightly soluble in cold, more in boiling, water; readily in alcohol or ether, especially on heating. It dissolves in hot nitric acid, and crystallises on cooling. Cold sulphuric acid dissolves it unaltered, but decomposes it when heated strongly. Sulphide of ammonium and other reducing agents convert it into diamidobenzoic acid. The alkaline *dinitrobenzoates* are soluble and crystallisable: the *lead-* and *silver-salts* are slightly soluble. *Dinitrobenzoic ether* (dinitrobenzoate of ethyl), $C^9H^8N^2O^6 = C^7H^3(C^2H^5)(NO^2)^2O^2$, is obtained by saturating absolute alcohol with the acid, or heating the acid with alcohol and sulphuric acid: it forms oily drops, which solidify on cooling, and are washed with dilute ammonia, and crystallised from hot alcohol. Long delicate needles, with a slight yellow tinge: decomposed by strong potash, especially on heating, into alcohol and potassic dinitrobenzoate. Digestion with alcoholic ammonia converts it into dinitrobenzamide: sulphuretted hydrogen converts it into diamidobenzoic acid. (Voit.)

Nitrochlorobenzoic Acid. $C^7H^4NClO^4 = C^7H^4(NO^2)ClO^2$ (Limpricht and v. Uslar, Ann. Ch. Pharm. cii. 261).—When chlorobenzoic acid is dissolved in fuming nitric acid, there is no immediate precipitate, but the solution continues for several days to deposit colourless tables of nitrochlorobenzoic acid. These melt at 118° C.; are soluble in alcohol and ether; melt in warm water, dissolve on boiling, and do not separate out on cooling. The *barium-* and *silver-salts* only are known: the latter, $C^7H^3AgClNO^4 + \frac{1}{2}$ Aq (?), forms small shining laminæ, tolerably soluble in water. For *nitrochlorobenzoic ether*, see above, *chlorobenzoic ether*. F. T. C.

BENZOIC ALCOHOL. Syn. with BENZYLIC ALCOHOL (*q. v.*)

BENZOIC ANHYDRIDE. *Benzoate of Benzoyl.* $C^{14}H^{10}O^3 = (C^7H^5O)^2.O$ (Gerhardt (1852), Ann. Ch. Phys. [3] xxxvii. 299; Wunder, J. pr. Chem. lxi. 498; Heintz, Pogg. Ann. xcii. 458).—Formed by the action of chloride of benzoyl on alkaline oxalates or benzoates: also of oxychloride or perchloride of phosphorus, or chloride of sulphur on alkaline benzoates, the first stage of the reaction being the formation of chloride of benzoyl: also by the dry distillation of acetobenzoic and similar anhydrides:

$$\begin{aligned}
C^7H^5KO^2 + C^7H^5OCl &= C^{14}H^{10}O^3 + KCl.\\
C^2O^4K^2 + 2C^7H^5OCl &= C^{14}H^{10}O^3 + 2KCl + CO + CO^2.\\
2C^7H^5KO^2 + PCl^5 &= C^{14}H^{10}O^3 + 2KCl + POCl^3\\
8C^7H^5KO^2 + 3SCl^2 &= 4C^{14}H^{10}O^3 + 6KCl + SO^4K^2 + S^2.
\end{aligned}$$

Equal parts of dry benzoate of sodium and chloride of benzoyl are heated to 130° C. on a sand-bath, whereby a clear liquid is produced, from which chloride of sodium separates out: the cooled mass is washed with cold water containing sodic carbonate, and crystallised from ether or warm alcohol. The previous preparation of chloride of benzoyl is avoided by employing perchloride or oxychloride of phosphorus (5 pts. oxychloride to 1 pt. benzoate). Oxalate of potassium is heated with an equal weight of chloride of benzoyl, with constant agitation, till the smell of chloride of benzoyl has disappeared; and the cooled mass is suspended in cold water, washed with water containing ammonia, and crystallised from alcohol (Gerhardt). In preparing large quantities, it is better to purify the product by distillation than by crystallisation from alcohol.

Benzoic anhydride forms oblique rhombic prisms, sometimes smelling of bitter-almond oil or benzoic ether: it melts at 42° C., and distils undecomposed at about 310°. It is insoluble in cold water, soluble in alcohol and ether: the solution when fresh has no acid reaction. It melts in boiling water, and remains fluid for a long time, even when agitated, and is slowly converted into benzoic acid, which dissolves. Caustic alkalis convert it much more rapidly into benzoic acid. Aqueous ammonia does not attack it in the cold, but dissolves it on heating, forming benzamide and benzoate of ammonium: the same reaction takes place when it is heated in dry ammonia:

$$C^{14}H^{10}O^3 + 2NH^3 = C^7H^7NO + C^7H^5(NH^4)O^2.$$

Aniline acts similarly, forming phenylbenzamide. (Gerhardt.)

One atom of benzoyl in benzoic anhydride is capable of being replaced by other acid radicles, forming a series of anhydrides containing benzoyl. They are obtained by the action of chloride of benzoyl on the alkaline salts of other monobasic acids, or, conversely, by treating alkaline benzoates with the chlorides of monobasic acid radicles. They are generally decomposed by heat into two simple anhydrides: by water, and more rapidly by alkalis, into two acids.

Benzoacetic Anhydride. See Acetic Anhydride.

Benzoangelic Anhydride. $C^{12}H^{12}O^3 = C^5H^7O.C^7H^5O.O$ (Chiozza, Ann. Ch. Phys. [3] xxxix. 210).—Produced by gently heating chloride of benzoyl with angelate of potassium. It is a limpid oil, heavier than water, somewhat less fluid than angelic anhydride, and quite neutral to test-paper. It smells like angelic anhydride, but emits much more acrid vapours when heated. In a mixture of ice and salt, it thickens slightly, without crystallising.

Benzocinnamic Anhydride. *Benzoate of Cinnamyl.* $C^{16}H^{12}O^3 = C^7H^5O.C^9H^7O.O$ (Gerhardt, *loc. cit.*)—Obtained by heating 7 pts. chloride of benzoyl with 10 pts. dry cinnamate of sodium, and purifying the product as in the case of benzoic anhydride. It is a thick oil, colourless and odourless, which gradually becomes acid when exposed to moist air. Specific gravity 1·184 at 23° C. Is decomposed by distillation, yielding a yellow oil, smelling of cinnamol, which gradually deposits crystals of benzoic anhydride, and an acid substance soluble in sodic carbonate.

Benzocuminic Anhydride. *Benzoate of Cumyl.* $C^{17}H^{16}O^3 = C^7H^5O.C^{10}H^{11}O.O$ (Gerhardt, *loc. cit.*)—Obtained like the preceding, cuminate being substituted for cinnamate of potassium. Resembles the preceding in appearance and behaviour in moist air. Specific gravity 1·115 at 23° C. Is decomposed by distillation: when heated in a closed vessel, it appears to volatilise without decomposition. Aqueous ammonia converts it into cuminamide, and benzamide, or benzoate of ammonium.

Benzomyristic Anhydride. *Benzoate of Myristyl.* $C^{21}H^{32}O^3 = C^7H^5O.C^{14}H^{27}O.O$ (Chiozza and Malerba, 1855).—Obtained by heating chloride of benzoyl with myristate of potassium. Crystallises from boiling ether, in which it is slightly soluble, in shining laminæ: melts at 38°, and solidifies at 36° C.

Benzoœnanthylic Anhydride. *Benzoate of Œnanthyl.* $C^{14}H^{18}O^3 = C^7H^5O.C^7H^{13}O.O$ (Chiozza and Malerba, Ann. Ch. Pharm. xci. 102).—Obtained by the action of chloride of benzoyl on œnanthylate of potassium. Colourless oil, of specific gravity 1·043 at 11° C.; smells like œnanthylic anhydride: exposed to the air, it yields crystals of benzoic acid.

Benzopelargonic Anhydride. *Benzoate of Pelargonyl.* $C^{16}H^{22}O^3 = C^7H^5O.C^9H^{17}O.O$ (Chiozza, Ann. Ch. Phys. [3] xxxix. 310).—Prepared like the foregoing compounds. A heavy oil, resembling pelargonic anhydride. A little below 0° C. it solidifies to the consistency of butter: is decomposed by heat into benzoic and pelargonic anhydrides.

Benzostearic Anhydride. *Benzoate of Stearyl.* $C^{25}H^{40}O^3 = C^7H^5O.C^{18}H^{35}O.O$ (Chiozza and Malerba, *loc. cit.*)—Prepared by heating chloride of benzoyl and potassic stearate in an oil-bath. Shining scales, which melt at 70° C.

Benzovaleric Anhydride. *Benzoate of Valeryl.* $C^{12}H^{14}O^3 = C^7H^5O.C^5H^9O.O.$ (Chiozza, Ann. Ch. Pharm. lxxxiv. 106).—Chloride of benzoyl acts violently on valerate of potassium: the product is a heavy, neutral, strongly refracting oil, smelling like valeric anhydride. At about 260° C. it is decomposed into benzoic and valeric anhydrides.

Substitution-products of Benzoic Anhydride.

Benzonitrobenzoic Anhydride. *Benzoate of Nitrobenzoyl.* $C^{14}H^9NO^5 = C^7H^5O.C^7H^4(NO^2)O.O.$—3 pts. chloride of benzoyl are heated with 7 pts. dry nitrobenzoate of sodium, and the product is purified as in the case of benzoic anhydride. Crystalline: more stable than the following compound. (Gerhardt, *loc. cit.*)

Nitrobenzoic Anhydride. *Nitrobenzoate of Nitrobenzoyl.* $C^{14}H^8N^2O^7 = [C^7H^4(NO^2)O]^2.O.$ — 8 pts. nitrobenzoate of sodium are heated to 150° C. with 1 pt. oxychloride of phosphorus, till the smell of chloride of nitrobenzoyl has disappeared. On treating the product with cold water, a white mass is obtained, almost insoluble in alcohol and ether, less fusible than nitrobenzoic acid, into which it is quickly converted by washing with water. (Gerhardt, *loc. cit.*) F. T. C.

BENZOIC ETHERS. See p. 552.

BENZOICIN. (Berthelot, Ann. Ch. Phys. [3] xli. 290.)—The name given by Berthelot to the artificial fats obtained by the action of benzoic acid on glycerin. Glycerin being a triatomic alcohol, $C^3H^5.H^3.O^3$, contains 3 at. H replaceable by other radicles; and Berthelot has succeeded in obtaining the compounds in which 1 and 3 H respectively are replaced by benzoyl.

Monobenzoicin. *Benzoate of Glycyl.* $C^{10}H^{12}O^4 = C^3H^5.C^7H^5O.H^2.O^3$. — Obtained by heating benzoic acid with glycerin in a sealed tube, for forty-four hours, to 120°—150° C. if the acid be in excess, to 200° C. if the glycerin be in excess; at a higher temperature a shorter time suffices. The product is purified by washing with potassic carbonate. It is a colourless, neutral, very viscid oil, with a bitter aromatic taste, and a slight balsamic smell; specific gravity 1·228 at 16°·5 C. At 40° it is a transparent nearly solid mass, that can be drawn out into threads; it boils at 320°, but decomposes at the same time, yielding acrolein and benzoic acid. It is insoluble in water, scarcely soluble in bisulphide of carbon, readily in alcohol, ether and benzene. It oxidises very slightly in the air. Heated with potash it forms potassic benzoate; with ammonia, benzamide. Alcohol and hydrochloric acid convert it in the cold into glycerin and benzoate of ethyl; the same decomposition is effected when its alcoholic solution is heated to 100° C. for forty-eight hours.

Tribenzoicin. *Tribenzoate of Glycyl.* $C^{24}H^{20}O^6 = C^3H^5.(C^7H^5O)^3.O^3$. — Obtained by heating monobenzoicin for four hours to 250° C., with 10 or 15 pts. benzoic acid; the product is washed with sodic carbonate, and repeatedly crystallised from ether. Large white needles, unctuous to the touch, and fusing pretty readily. Alcohol and hydrochloric acid decompose it like monobenzoicin. F. T. C.

BENZOIN. *Bitter-almond-oil-camphor.* $C^{14}H^{12}O^2$. (Liebig and Wöhler, Ann. Ch. Pharm. iii. 276; Robiquet and Boutron-Charlard, Ann. Ch. Phys. [2] xliv. 352; Laurent, *ibid.* lix. 402; lxvi. 193; Zinin, Ann. Ch. Pharm. xxxiv. 186.) —First described by Stange, 1823 (Repert. Pharm. xiv. 329); first correctly examined by Liebig and Wöhler in 1832. It is frequently contained in crude bitter-almond oil, and is obtained as a by-product when the oil is purified by lime and ferrous chloride; the residue is treated with dilute hydrochloric acid, and dissolved in alcohol. Pure bitter-almond oil (hydride of benzoyl) is converted into benzoin by cyanide of potassium. To prepare benzoin from crude bitter-almond oil, the oil is mixed with its own volume of a saturated alcoholic solution of potash; after a few minutes, the whole solidifies to a mass of crystals, which are purified by recrystallisation from alcohol. As the amount of benzoin in different specimens of the crude oil varies considerably, according to their age and to the amount of prussic acid which they contain, it is always advisable to test a small portion first with alcoholic potash; if it does not speedily solidify, the crude oil had better be first freed from prussic acid, and then treated by the ensuing method. Pure oil of bitter-almonds is readily converted into benzoin by the addition of a dilute alcoholic solution of cyanide of potassium, or of alcoholic potash to which a few drops of hydrocyanic acid have been added: this reaction is difficult to account for.

Benzoin is isomeric with benzoate of benzyl, and polymeric with hydride of benzoyl. It forms shining, transparent, colourless prisms, without smell or taste; melts at 120° C., and crystallises on cooling; if further heated, it distils undecomposed. It is insoluble in cold, slightly soluble in hot water, whence it crystallises on cooling; more soluble in hot than in cold alcohol. It burns readily in the air, with a bright smoky flame. Its vapour passed through a red-hot tube is reconverted into hydride of benzoyl. When heated in *chlorine*, it yields benzil and hydrochloric acid. *Bromine* attacks it, evolving hydrobromic acid, and forming (probably) benzil. Strong *nitric acid* converts it into benzil. *Sulphuric acid* dissolves it, forming a violet solution, which blackens when heated. Boiling *potash* does not attack it; fused with solid potash, it evolves hydrogen and yields benzoic acid: $C^{14}H^{12}O^2 + 2KHO = 2C^7H^5KO^2 + H^4$; boiled with alcoholic potash, it is coloured violet, and yields benzilic acid, with evolution of hydrogen: $C^{14}H^{12}O^2 + KHO = C^{14}H^{11}KO^3 + H^2$. With *ammonia*, it yields, among other products, benzoinam and benzoinamide. *Perchloride of phosphorus* attacks it violently, yielding chloride of phosphoryl, and other products difficult to obtain pure. (Cahours.)

Benzoin combines with chlorides of acid radicles, yielding compounds representing benzoin in which 1 H is replaced by an acid radicle. Zinin (Ann. Ch. Pharm. civ. 116) has obtained the following: —

Acetyl-benzoin. $C^{16}H^{14}O^3 = C^{14}H^{11}(C^2H^3O)O^2$.—4 pts. of benzoin dissolve in 3 pts. chloride of acetyl at 40° – 50° C., with evolution of hydrochloric acid; when the solution is complete, the whole is heated to 100° as long as vapours are evolved: on cooling, the product slowly solidifies into crystals, which are recrystallised from alcohol or ether. It crystallises from the ethereal solution in large rhombic prisms and six-sided tables; from the alcoholic solution in thin shining crystals. It is insoluble in water, melts below 100°, and does not always crystallise on cooling. Sulphuric or hydrochloric acid, or aqueous potash does not act upon it; with alcoholic potash it yields acetate and benzoate of potassium. Strong nitric acid converts it into a mixture of two nitro-products in the form of a viscid colourless mass, insoluble in water, soluble in alcohol and ether; the solution deposits crystals.

Benzoyl-benzoin. $C^{21}H^{16}O^3 = C^{14}H^{11}(C^7H^5O)O^2$.—Chloride of benzoyl does not act upon benzoin in the cold, but at about 70° C. the benzoin dissolves and hydrochloric acid is evolved; the whole is then heated to nearly the boiling point of chloride of benzoyl (196° C.), when a yellowish oily liquid is obtained, which solidifies into crystals on cooling. This product is purified by being poured while liquid into cold 75 per cent. alcohol, when benzoyl-benzoin separates as a crystalline powder, which is washed on a filter with cold alcohol. It is insoluble in water, sparingly soluble in cold alcohol, soluble in 6 pts. boiling 80 per cent. alcohol, whence it crystallises in thin colourless needles; readily soluble in ether, and crystallises by spontaneous evaporation in large shining rhombic prisms; soluble in chloride of benzoyl, and may be heated with it to 150° C. without alteration. Melts at 125° C., and crystallises very slowly on cooling. Chlorine does not attack it, neither does hydrochloric or dilute sulphuric acid; strong sulphuric acid decomposes it. Aqueous potash does not attack it; alcoholic potash dissolves it with a violet colour, and, on boiling, converts it into benzoate and benzilate of potassium.

Nitrobenzoyl-benzoin. $C^{21}H^{15}NO^5 = C^{14}H^{11}(C^7H^4(NO^2)O)O^2$.—Strong nitric acid (specific gravity 1·51) dissolves benzoyl-benzoin, which, if too little acid be employed, crystallises out again unaltered; but if at least 1½ pt. acid be taken, and the yellowish solution poured into cold water, a resinous substance separates, which is a mixture of two nitro-products. Ether dissolves one of these, and abandons it on evaporation as a thick oil; the other, which is nitrobenzoyl-benzoin, remains undissolved as a crystalline powder, which is recrystallised from boiling alcohol. White shining scales, composed of rhombic tables, aggregated into scalariform groups, insoluble in water. Melts at 137° C., and solidifies at 110° to an amorphous mass, which very slowly becomes crystalline. Strong nitric acid dissolves it unaltered and in large quantities, especially if gently heated; on boiling the solution a new body is formed, soluble in ether, which separates as a powder on cooling. F. T. C.

BENZOINAM. $C^{28}H^{24}N^2O$. (Laurent, Compt. Chim. [1845] 37).—Formed by the action of alcoholic ammonia on benzoin:

$$2C^{14}H^{12}O^2 + 2NH^3 = C^{28}H^{24}N^2O + 3H^2O.$$

Obtained, together with benzoinamide and other products, when a mixture of alcoholic ammonia and benzoin is left for some months in a closed vessel. Forms white microscopic inodorous needles, insoluble in water; slightly soluble in hot ether or rock-oil, whence it crystallises on cooling in very bulky needles, readily soluble in hot alcohol containing hydrochloric acid, whence it is partially precipitated by water, entirely by ammonia. Melts when heated, and partly solidifies on cooling. Potash does not attack it; strong sulphuric acid dissolves it with red colour, and water precipitates orange flakes. F. T. C.

BENZOINAMIDE. $C^{42}H^{36}N^4$. (Laurent [1837], Ann. Ch. Phys. [2] lxvi. 189.)—Formed by the action of aqueous ammonia on benzoin:

$$3C^{14}H^{12}O^2 + 4NH^3 = C^{42}H^{36}N^4 + 6H^2O.$$

Obtained as a white powder when benzoin and aqueous ammonia are left for eight weeks in a closed vessel; it is boiled in alcohol to remove excess of benzoin, and crystallised from boiling ether. A white, tasteless, odourless powder, consisting of fine microscopic needles; insoluble in water, very sparingly soluble in alcohol or ether; melts when heated, and solidifies to a fibrous mass; distils without decomposition.

F. T. C.

BENZOIN-GUM. The commercial name of a resin which flows from the bark of *Styrax benzoin*, a tree growing in Sumatra, Borneo, Java, and Siam. It comes into the market in different forms. The Siamese gum occurs in irregular flat fragments, about an inch long, which are reddish-yellow on the outside, white and shining in the inside. The common or Calcutta-gum forms larger irregular lumps, brittle, of a dirty reddish-grey or brown colour, with many light coloured spots, and often contains fragments of wood and bark. The Siamese almond-gum appears to be a mixture of both these kinds. The commercial gum has a pleasant smell, especially when heated, and a sweetish, sharp, balsamic taste. It melts when heated, evolves vapours of benzoic acid, and burns with a smoky flame. Specific gravity 1·063—1·092. Alcohol dissolves it completely, excepting impurities; ether partially; boiling water dissolves out benzoic acid.

According to Unverdorben (Pogg. Ann. viii. 397), Stolze (Berl. Jahrb. Pharm. xxvi. 75), Van der Vliet (Ann. Ch. Pharm. xxxiv. 177), and E. Kopp (Compt. rend. xix. 1269), gum-benzoin is a mixture of three resins, which may be distinguished as α, β, and γ, together with benzoic acid, and a small quantity of a volatile oil. The whole of the benzoic acid cannot be driven off by heat. According to Kolbe and Lautemann (Ann. Ch. Pharm. cxv. 113), some varieties of gum-benzoin, especially the almond gum of Sumatra, contain not benzoic acid, but an acid isomeric with toluylic acid, $C^8H^8O^2$, which melts to a clear liquid under hot water, crystallises in forms quite different from that of benzoic acid, and yields hydride of benzoyl when treated with oxidising agents.

Unverdorben separates the resins in the following manner:—The powdered gum is extracted with boiling sodic carbonate, which dissolves out all the benzoic acid and the resin γ; the alkaline solution is precipitated by hydrochloric acid, and the precipitate treated with boiling water, which dissolves the acid only, leaving the resin γ insoluble. The portion insoluble in sodic carbonate is washed, dried, and digested with ether, which dissolves the resin α, and leaves the resin β undissolved. According to Kopp, the ethereal solution of α gradually deposits a small quantity of a fourth resin, δ, of a reddish-brown colour. Analyses of two specimens of gum gave the following results (Kopp):

	I.	II.
Benzoic acid	14·0	14·5
Resin α	52·0	48·0
Resin β	25·0	28·0
Resin γ	3·0	3·5
Resin δ	0·8	0·5
Impurities	5·2	5·5

Kopp further states that the white spots in the gum are composed only of resin α, and contain 8—12 per cent. benzoic acid; while the brown portions consist of resins β and γ, and contain as much as 15 per cent. acid (18 per cent. according to Unverdorben).

The resin α is readily soluble in ether and alcohol, insoluble in naphtha; soluble in potash, and not reprecipitated by excess; insoluble in ammonia. Salts of the earthy or heavy metals give, in its alkaline solution, precipitates which are insoluble in ether. According to Van der Vliet it is a mixture of resins β and γ, for it is decomposed into these two resins by prolonged ebullition with sodic carbonate. Resin β is a brownish mass, soluble in alcohol, insoluble in ether and volatile oils; soluble in potash, and reprecipitated by excess; insoluble in ammonia. Resin γ is dark-brown, soluble in alcohol, slightly in ether and volatile oils, insoluble in naphtha. Potassic carbonate slowly dissolves it, and the solution is precipitated by sal-ammoniac. Its alcoholic solution precipitates acetate of lead, but not acetate of copper. Resins α and β, when precipitated by acids from their alkaline solutions, are converted into γ by exposure to the air.

The following are the results of the analysis of these resins, and the (unreliable) formulæ, which Van der Vliet has deduced therefrom:

		V. d. V.		Mulder.	
Resin α	Carbon	72·9	71·8	73·1	$C^{35}H^{42}O^7 = \beta + \gamma$
	Hydrogen	7·2	7·1	7·3	
Resin β	Carbon	71·1	71·0	71·7	$C^{20}H^{21}O^{4\frac{1}{2}}$
	Hydrogen	6·2	6·3	6·9	
Resin γ	Carbon	73·2	73·2	73·2	$C^{15}H^{21}O^{2\frac{1}{2}}$
	Hydrogen	8·6	8·4	8·6	

By the dry distillation of the resins of gum-benzoin, completely freed from benzoic acid, Kopp obtained a solid substance, which he regards as the odorous principle of the gum, and a rose-red distillate, which gradually becomes darker, and contains crystals of benzoic acid; the fluid portion appears to be hydrate of phenyl. By the same process, Cahours obtained an oil, which Deville (Ann. Ch. Phys. [3] iii. 192) regards as benzoate of ethyl. When they are distilled to dryness, with excess of nitric acid, nitrous fumes are abundantly evolved, and a distillate is obtained, containing hydride of benzoyl, benzoic acid, and hydrocyanic acid; boiling water extracts picric acid from the residue, and leaves a yellow powder, *benzoeretic acid* (*q. v.*) Sulphuric acid dissolves the resins to a common solution, whence the addition of water separates them almost completely as a violet precipitate; the acid liquid, decanted and neutralised with lime yields a soluble calcium-salt. F. T. C.

BENZOLACTIC ACID. *Benzomilchsaure.* $C^{10}H^{10}O^4 = C^3H^4O.C^7H^5O.H.O^2$ (Socoloff and Strecker, Ann. Ch. Pharm. lxxx. 46. Strecker *ibid.* xci. 359).—This acid is analogous to benzoglycollic acid, representing lactic acid in which 1 at. of of basic hydrogen is replaced by benzoyl, just as benzoglycollic acid represents glycollic acid in which 1 at. of basic hydrogen is similarly replaced.

It is prepared by heating 10 pts. of syrupy lactic acid with 14 pts. of benzoic acid in an oil-bath to 150° C., finally raising the temperature to 200°, and keeping it there for some hours. Water distils over, and some benzoic acid sublimes. The residue in the retort solidifies on cooling to a crytsalline mass of benzoic and benzolactic acids. These are separated by partial saturation with sodic carbonate, which takes up the benzolactic acid first; the solution is filtered from the benzoic acid, and freed from the small quantity of benzoic acid which it contains by agitation with ether; on the addition of hydrochloric acid, benzolactic acid separates in crystals, which are purified by recrystallisation from boiling water, or from ether-alcohol.

It forms colourless tabular or spear-shaped crystals, unctuous to the touch: melts at 112° C., and solidifies very slowly on cooling to a crystalline mass; sublimes undecomposed when heated considerably above 120°. It dissolves in 400 pts. cold, and in much less boiling water: when boiled with not enough water to dissolve it, the excess of acid melts and the solution becomes milky on cooling, and clarifies very slowly, with separation of crystals. It dissolves readily in alcohol or ether, the latter removing it entirely from its aqueous solution; after drying in the air, it does not lose any water when heated to melting. By prolonged boiling in water, it is decomposed with benzoic and lactic acids: the decomposition is accelerated by the addition of a dilute acid.

The *benzolactates* are mostly crystalline, soluble in water, and closely resemble the benzoates, from which, however, they are distinguished by their neutral solution not being precipitated by normal acetate of lead. The *barium-salt*, $C^{10}H^9BaO^4 + 3\,aq.$, crystallises in thin, shining, six-sided laminæ, which lose their water at 100° C. The *silver-salt* $C^{10}H^9AgO^4$, is a flocculent precipitate, soluble in boiling water, whence it crystallises in fine needles. The *sodium-salt* crystallises in colourless needles from boiling alcohol. F. T. C.

BENZOLIC ALCOHOL. See BENZYLENE.

BENZOLINE. Syn. with AMARINE (*q.v.*)

BENZOLONE. $C^{21}H^{15}O^2$ (?) (Rochleder, Ann. Ch. Pharm. xli. 94).—Formed together with benzostilbin, when hydrobenzamide is heated with solid potash. The mixture must be heated till it blackens; the product is powdered, extracted with water, washed with cold hydrated alcohol, and the residue dissolved in strong sulphuric acid. The blood-red solution thus formed becomes greenish-yellow on addition of dilute alcohol, and deposits small crystals of benzolone: on addition of water, it separates in the uncrystalline state. It is insoluble in water or alcohol; melts at 248° C., and sublimes almost without decomposition, when more strongly heated. Strong nitric acid dissolves it with a reddish-yellow colour, and it is reprecipitated by water; fuming nitric acid decomposes it, forming a yellowish resin with evolution of nitrous fumes. It is not attacked by aqueous potash. Rochleder's analyses give a mean composition of C 83·5, H 5·2. F. T. C.

BENZOMERCURAMIDE. See BENZAMIDE.

BENZOMYRISTIC ANHYDRIDE. See BENZOIC ANHYDRIDE.

BENZONE. *Benzophenone. Phenyl-benzoyl.* $C^{13}H^{10}O = C^6H^5.C^7H^5O$ (Péligot, Ann. Ch. Phys. [2] lvi. 59. Chancel, Compt. rend. xviii. 83.; Ann. Ch. Pharm. lxxx. 25).—The acetone of benzoic acid; it is formed by the dry distillation of benzoate of calcium:

$$2C^7H^5CaO^2 = C^{13}H^{10}O + CO^3Ca^2.$$

Dry benzoate of calcium is mixed with $\frac{1}{10}$ of its weight of quick lime, and distilled in an iron mercury bottle, fitted with a bent gun-barrel. The red liquid which passes over (which Péligot called benzone), contains,—besides benzone,—benzene, hydride of benzoyl, and two solid hydrocarbons isomeric with naphthalin. On distilling it in a tubulated retort, benzene first passes over; and the temperature rises rapidly: the portion which comes over at 315°—325° C. is collected apart, and consists of nearly pure benzone, which solidifies on cooling, and may be obtained quite pure by recrystallisation from ether-alcohol. 1 kilogr. benzoate of calcium yields about 250 grms. benzone.

Benzone forms colourless, transparent crystals, often of considerable size, belonging to the trimetric system. It melts at 46° C. to a thick oil which does not solidify unless it be agitated; boils at 315° and distils undecomposed: its vapour is very inflammable, and burns with a bright flame. It has a pleasant smell, somewhat like that of benzoic ether. It is very soluble in ether, less so in alcohol, not at all in water; strong nitric or sulphuric acid dissolves it abundantly, and water reprecipitates it unchanged. When heated with soda-lime to about 260° C. it is decomposed, yielding sodic benzoate and benzene, but not a trace of hydrogen:

$$C^6H^5.C^7H^5O + NaHO = C^6H^5.H + C^7H^5O.Na.O.$$

Dinitrobenzone. Dintrobenzophenone. $C^{13}H^8N^2O^5 = C^{13}H^8(NO^2)^2O$.—Warm fuming nitric acid converts benzone into a thick oil, which solidifies very slowly; ether dissolves it and deposits it speedily in the form of a yellowish crystalline powder, which is dinitrobenzone. Reducing agents convert it into diphenyl-carbamide (flavine):

$$C^{13}H^{8}N^{2}O^{5} + 6H^{2}S = \underset{\text{flavine.}}{C^{13}H^{12}N^{2}O} + 4H^{2}O + S^{6}.$$

Of the two hydrocarbons, isomeric with naphthalin, mentioned above, one crystallises in large needles, fusible at 92° C., the other, much less soluble in alcohol and ether, forms small nodules fusible at 65°. The former is readily obtained by dissolving in strong sulphuric acid the liquid obtained by the dry distillation of calcic benzoate; it immediately solidifies on the surface, and is removed, washed, dried by filter paper, and crystallised from hot alcohol. The latter is best prepared by the dry distillation of potassic benzoate with potash-lime: it then passes over alone, in solution in benzol, which is distilled off in a water-bath, and the residue crystallised from alcohol. It is also formed together with benzol, when ammonic benzoate is passed over heated baryta. F. T. C.

BENZONITRILE. *Cyanide of Phenyl.* $C^{7}H^{5}N = C^{6}H^{5}.CN$ (Fehling (1844), Ann. Ch. Pharm. xlix. 91. Limpricht and v. Uslar, *ibid.* lxxxviii. 133).—Benzonitrile is obtained by various methods:—1. By the dry distillation of benzoate of ammonium, or by heating benzamide, either alone or with caustic lime, or baryta, phosphoric anhydride, or perchloride of phosphorus: the reaction in all these cases consists in the abstraction of the elements of water:

$$\underset{\text{Benz. amm.}}{C^{7}H^{5}O.NH^{4}.O} - 2H^{2}O = C^{7}H^{5}N.$$

$$\underset{\text{Benzamide.}}{N.C^{7}H^{5}O.H^{2}} - H^{2}O = C^{7}H^{5}N.$$

2. By heating hippuric acid, either alone (Limpricht), or with chloride of zinc (Gössmann). 3. By the action of chloride of benzoyl or benzoic anhydride on benzamide, or by heating benzamide with potassium (see BENZAMIDE). 4. By the action of chloride of benzoyl on oxamide (Chiozza):

$$C^{7}H^{5}O.Cl + N^{2}.C^{2}O^{2}.H^{4} = C^{7}H^{5}N + CNH + HCl + CO^{2} + H^{2}O.$$

or on sulphocyanate or cyanate of potassium (Schiff, Ann. Ch. Pharm. xcix. 117, ci. 93):

$$2C^{7}H^{5}O.Cl + 2CNSK = 2C^{7}H^{5}N + 2KCl + CO^{2} + CS^{2}.$$

5. By heating benzoic anhydride with cyanate or sulphocyanate of potassium (Schiff):

$$C^{14}H^{10}O^{3} + 2CNOK = 2C^{7}H^{5}N + CO^{3}K^{2} + CO^{2}.$$

6. By the action of mercuric oxide on thiobenzamide (*q. v.* under BENZAMIDE).

Preparation.—1. When dry benzoate of ammonium is heated in a retort, ammonia escapes, benzoic acid sublimes, and water passes over with a few oily drops of benzonitrile; as most of the benzonitrile remains in the fused residue in the retort, this is covered with water (to which a little ammonia is added), again distilled to dryness, and the operation repeated as long as any oil passes over with the water: 12 oz. benzoic acid yield in 5 days, 6 oz. impure benzonitrile. This product is washed with dilute hydrochloric acid, then with water, dried over chloride of calcium, and rectified (Fehling). According to Laurent and Chancel (Compt. chim. 1849, 117), benzonitrile is more easily prepared by passing the vapour of ammonic benzoate over heated baryta.—2. One pt. dry hippuric acid is mixed in a warm mortar with an equal bulk of quartz-sand and 2 pts. chloride of zinc dried as completely as possible, and the mixture is heated in a dry retort to 300°—350°C.: benzontrile then distils over, carbonic anhydride escapes, and a little carbon is deposited; 100 grms. hippuric acid (the utmost precautions being taken to exclude moisture) yielded 33—40 grms. benzonitrile; calculation requires 57 grm. (Gössmann, Ann. Ch. Pharm. c. 72).—3. According to Buckton and Hofmann, benzonitrile is best prepared by distilling benzamide with phosphoric anhydride.

Benzonitrile is a clear, colourless, strongly refracting oil, smelling like bitter-almond oil, and having a burning taste; specific gravity 1·0230 at 0°, 1·0084 at 16·8° C. Kopp). At higher temperatures it is less dense than water, for it sinks in cold water, but rises to the surface when heated. It boils at 190·6° C. with the barometer at 733·4 mm. (Kopp), and distils undecomposed: its vapour density is 3·7 (expt.); its coefficient of refraction is 1·503 (Reusch). It dissolves in 100 pts. boiling water, and separates out again on cooling; it mixes with alcohol and ether in all proportions. Sulphur dissolves in it with the aid of heat, and crystallises out on cooling.

Benzonitrile burns with a bright smoky flame. Cold *aqueous potash* does not attack it, but on boiling, ammonia is evolved and potassic benzoate formed; a similar decomposition is effected by dilute acids. Strong *sulphuric acid* dissolves it, and on heating, sulphobenzoic and disulphobenzolic acids, and acid sulphate of ammonium are formed, and carbonic anhydride is evolved: (Buckton and Hofmann):

$$2C^7H^5N + 5SO^4H^2 + H^2O = C^7H^6SO^5 + C^6H^6S^2O^6 + 2(NH^4.H.SO^4.) + CO^2.$$

With fuming *nitric acid* it forms a substitution-product (see below); when heated with potassium in a sealed tube, it assumes a carmine colour, and at 240° C. yields a sublimate of fine needles; water extracts cyanide of potassium from the product, and the residue yields on distillation, a green oil smelling of creosote, in which crystals again form (Bingley, Chem. Gaz. 1854, 329). With *sulphide of ammonium*, it forms *thiobenzamide* (*q. v.* under BENZAMIDE).

Substitution-products of Benzonitrile.

Chlorobenzonitrile or *Cyanide of Chlorophenyl*, C^7H^4ClN, has not been obtained by the action of chlorine on benzonitrile; but it is the principal product when sulphobenzamide or sulphobenzamic acid is distilled with perchloride of phosphorus. The distillate is mixed with potash, and rectified, when chlorobenzonitrile passes over with aqueous vapour, and collects in the receiver, forming crystals which are obtained in large colourless prisms by recrystallisation from alcohol or ether. It smells like bitter-almond oil, is insoluble in water, but readily soluble in alcohol or ether; melts below 40°, and solidifies at 36° C., volatilises slightly at the ordinary temperature, more rapidly at a gentle heat. Prolonged boiling with dilute nitric acid converts it into chlorobenzoic acid; heated to 100° with ammonia in a sealed tube, it yields chlorobenzamide. (Limpricht.)

Nitrobenzonitrile or *Cyanide of Nitrophenyl.* $C^7H^4N^2O^2 = C^6H^4(NO^2)N$.—Precipitated as a white solid body when benzonitrile is heated gently with fuming nitric acid and water added to the solution; it is tolerably soluble in hot water, and separates on cooling in small white silky needles, soluble in acids, and reprecipitated by water. When heated, it evolves irritating vapours, and leaves a residue of carbon. When boiled with acids or alkalis, it yields ammonia and a nitrobenzoate. It cannot be obtained by the dry distillation of nitrobenzoate of ammonium (Gerland). F. T. C.

BENZONITROBENZOIC ANHYDRIDE. See BENZOIC ANHYDRIDE.

BENZONITROCUMIDE. See CUMYLAMINE.

BENZOŒNANTHYLIC ANHYDRIDE. See BENZOIC ANHYDRIDE.

BENZOPELARGONIC ANHYDRIDE. See BENZOIC ANHYDRIDE.

BENZOPHENIDE. Syn. with BENZOATE OF PHENYL. See BENZOIC ACID.

BENZOPHENONE. Syn. with BENZONE (*q. v.*)

BENZOPIPERIDE. See PIPERIDINE.

BENZOPROPYLENYL. Syn. with BENZOATE OF ALLYL. See BENZOIC ACID.

BENZOSALICIN. Syn. with POPULIN (*q. v.*)

BENZOSALICYLAMIC ACID. *Benzosalicylamide.* $C^{14}H^{11}NO^3 = N.H.C^7H^5O.C^7H^4O.H.O.$ (Gerhardt and Chiozza, Compt. rend. xxxvii. 86; Limpricht, Ann. Ch. Pharm. xciv. 249.)—When equivalent quantities of salicylamic acid and chloride of benzoyl are heated together to 120—145° C., as long as hydrochloric acid escapes, the product remains liquid a long time after cooling, but crystallises on adding a few drops of alcohol or ether; it is washed with ether, and dissolved in boiling alcohol, whence it crystallises in slender needles united in flocks. It is sparingly soluble in alcohol, even on boiling. When heated, it gives off water, and is converted into benzosalicylimide. It is readily soluble in ammonia, and is reprecipitated unchanged on evaporating the solution, or on addition of an acid. It dissolves in the fixed alkalis, forming deep yellow solutions, but is generally decomposed into benzoate and salicylate. It is attacked by chloride of benzoyl, yielding a crystalline product, which appears to be converted into benzosalicylamic acid by the addition of water or alcohol. After fusion, it is no longer completely soluble in hot ammonia; the yellow residue is soluble in alcohol, forming a yellow solution which deposits on evaporation small crystals, apparently of an ammonium-salt: the solution is decolorised by hydrochloric acid.

Benzosalicylamates.—The ammoniacal solution of the acid forms a light-yellow precipitate with normal acetate of lead, and a light-blue with sulphate of copper. With nitrate of silver, it forms the *silver-salt*, $C^{14}H^{10}AgNO^3$, a yellow precipitate, which becomes heated on contact with chloride of benzoyl, forming a viscous product, which dissolves in alcohol, leaving a residue of chloride of silver.

If salicylic acid be regarded as monobasic, this compound becomes *benzosalicylamide*, $N.C^7H^5O.C^7H^4O.^2H$. F. T. C.

BENZOSALICYLAMIDE. See BENZOSALICYLAMIC ACID.

BENZOSALICYLIC ACID. $C^{14}H^{10}O^4 = C^7H^4O.C^7H^5O.H.O^2$. (Gerhardt (1852), Ann. Ch. Phys. [3] xxxvii. 322.)—Formed by the action of chloride of benzoyl on salicylate of potassium, as a viscous mass difficult to purify, soluble in ether, decomposed by boiling water into benzoic and salicylic acids. By dry distillation, it yields benzoate of phenyl, and other products soluble in potash.

This compound is analogous to benzoglycollic and benzolactic acids. If salicylic acid be regarded as monobasic, it becomes benzosalicylic anhydride, $C^7H^5O.C^7H^5O^2.O$. F. T. C.

BENZOSALICYLIMIDE. See BENZAMIDE.

BENZOSTEARIC ANHYDRIDE. See BENZOIC ANHYDRIDE.

BENZOSTILBIN. $C^{14}H^{10}O$ (?) (Rochleder, Ann. Ch. Pharm. xli. 93).—The yellow powder obtained by fusing hydrobenzamide with solid potash consists of a mixture of three substances, a peculiar yellow oil, benzostilbin, and benzolone: the proportions of these three compounds vary with the duration of the fusion, benzolone not being formed at all unless the mixture has been heated till it blackens. The two former are separated from the third by alcohol, in which benzolone is insoluble. The alcoholic solution is mixed with a little hydrochloric acid, when it becomes red, but is decolorised by standing, and deposits benzostilbin in small crystals; the same result is produced more rapidly by passing chlorine into the solution. The crystals may be obtained larger by the slow evaporation of their solution in ether. When quite free from the yellow oil, they are but slightly soluble in alcohol. They melt at 244·5° C., and sublime when further heated, being in great measure decomposed. They dissolve with a red colour in sulphuric acid, and may be boiled without decomposition in aqueous potash of 1·2 specific gravity. Rochleder's analysis gives 86·5—86·6 C, 5·2—5·3 H. F. T. C.

BENZOSUCCININ. $C^{14}H^{12}O^6$. — The name given by Van Bemmelen (J. pr. Chem. lxix. 84) to a glyceride or artificial fat obtained by heating glycerin to 200° C. with benzoic and succinic acids. It is a soft dark-brown mass, which is decomposed by long boiling with water or alcohol, more rapidly in presence of an alkali, into benzoate and succinate. It represents glycerine in which 1 at. H is replaced by benzoyl and 2 at. by succinyl, $C^3H^5(C^7H^5O)(C^4H^4O^2)O^3$. F. T. C.

BENZOSULPHOPHENAMIC ACID. See BENZAMIDE.

BENZOSULPHOPHENAMIDE. See BENZAMIDE

BENZOSULPHOPHENAMIDYL, CHLORIDE, and AMIDE. See BENZAMIDE.

BENZOSULPHOPHENARGENTAMIDE. See BENZAMIDE.

BENZOSULPHOPHENYLSODAMIDE. See BENZAMIDE.

BENZOSYLANILIDE. See BENZYLENE-PHENYLAMINE.

BENZOTARTARIC ACID. $C^{11}H^{10}O^7 = (C^4HO^4)''.C^7H^5O.H.O^2$. (Dessaignes, J. de Pharm. [3] xxxii. 47.)—Obtained by heating a mixture of equivalent quantities benzoic and tartaric acids to 150° C. The acids melt at first without mixing, but at last form a homogeneous brown mass. When this is dissolved in boiling water, some benzoic acid crystallises out; the mother-liquor is partially neutralised by sodic carbonate, decolorised by animal charcoal, and acidulated with hydrochloric acid. After some time, nodular masses separate out, which are formed of microscopic crystals, and are not altered in form by recrystallisation. The acid is more soluble in cold water than benzoic acid, but less soluble in alcohol; its solution has no smell. No sublimate is formed when it is heated to the melting-point of benzoic acid; when it is further heated, benzoic acid sublimes, and the brown residue smells of heated tartaric acid. A cold saturated solution of the acid does not precipitate lime-water, ferric chloride, or nitrate of silver; it slightly precipitates a concentrated solution of normal acetate of lead. When neutralised with ammonia, it gives a pale yellow precipitate with ferric chloride, but does not precipitate chloride of calcium. When its solution is one-fourth neutralised with ammonia, it gives with nitrate of silver, a precipitate, which at first is redissolved: it contains 46·35 per cent. silver, corresponding to the formula $C^{11}H^8Ag^2O^7$. From this the acid would appear to be dibasic, in which case it is not analogous to benzoglycollic and benzolactic acids. F. T. C.

BENZOVALERIC ANHYDRIDE. See BENZOIC ANHYDRIDE.

BENZOYL. C^7H^5O.—The hypothetical radicle which, according to Liebig and

Wöhler's original suggestion, is usually considered as existing in benzoic acid and many of its kindred compounds,—benzoic acid, $C^7H^6O^2$, being regarded as hydrate of benzoyl, $C^7H^5O.H.O$, bitter-almond oil, C^7H^6O, as hydride of benzoyl, &c. This view explains the reactions of the majority of benzoyl-compounds in a far more satisfactory manner than that of Berzelius, who, in accordance with his opinion that oxygen never entered into the composition of an organic radicle, considered C^7H^5 as the radicle of this group of compounds. The readiness with which many benzoyl-compounds pass into phenyl-compounds renders it probable that benzoyl should be regarded as a compound of phenyl, C^6H^5, with carbonyl, CO; just as acetyl may be regarded as a compound of methyl and carbonyl. One or more atoms of hydrogen in benzoyl is capable of being replaced by a monatomic radicle (Cl, Br, NO^2, &c.) forming what may be called secondary or substitution-radicles (chlorobenzoyl, C^7H^4ClO, nitrobenzoyl, $C^7H^4(NO^2)O$, &c.), which may be supposed to exist in chloro- or nitro-benzoic acid, &c. Benzoyl has not yet been isolated. Benzil, which has the same composition, does not exhibit any analogy with other organic radicles. F. T. C.

BENZOYL, BROMIDE OF. *Brombenzaldid.* $C^7H^5O.Br$. (Liebig and Wöhler, Ann. Ch. Pharm. iii. 266.)—When hydride of benzoyl is mixed with bromine, heat is evolved, and hydrobromic acid given off: the mixture is then heated, to free it completely from hydrobromic acid and excess of bromine. Thus obtained, bromide of benzoyl is a soft, brown, broadly laminar, crystalline mass, semifluid at the ordinary temperature, and melting at a very gentle heat to a brownish-yellow liquid. It has a faint aromatic odour, somewhat like that of chloride of benzoyl, and is readily soluble, without decomposition, in alcohol and ether. When heated with water, it melts, and remains at the bottom, as a brownish oil, which is decomposed into benzoic and hydrobromic acids only by prolonged boiling. It fumes slightly in the air, strongly when heated, and burns with a bright sooty flame. F. T. C.

BENZOYL, CHLORIDE OF. *Chlorbenzaldid.* $C^7H^5O.Cl$. (Liebig and Wöhler (1832), Ann. Ch. Pharm. iii. 262; Cahours, Ann. Ch. Phys. [3] xxii. 334; Gerhardt, *ibid.* xxxvii. 291).—Formed: 1. by the action of chlorine on hydride of benzoyl (L. and W.)—2. By heating perchloride of phosphorus with benzoic acid (Cahours).—3. By the action of oxychloride of phosphorus on benzoates (Gerhardt). Also in small quantities, by the action of chlorine on mandelic acid, or on benzoate of methyl or ethyl (Malaguti, Ann. Ch. Phys. [2] lxx. 374), and on cinnamein (Fremy, *ibid.* 180).—4. By heating benzoic acid to 200° C. with a mixture of chloride of sodium and anhydrous acid sulphate of sodium or potassium.

Preparation.—1. Dry chlorine is passed into hydride of benzoyl, the liquid being gradually heated to boiling, till no more hydrochloric acid is evolved: the product is freed by heat from dissolved chlorine.—2. A better and easier method is to warm equivalent proportions of benzoic acid (122 pts.) and perchloride of phosphorus (209 pts.) in a tubulated retort; a violent reaction takes place, hydrochloric acid is evolved, and a mixture of chlorides of benzoyl and phosphoryl distils over, heat being gradually applied. The mixed chlorides are separated by fractional distillation: at 110° C., chloride of phosphoryl passes over; from 110° to 196°, a mixture of the two chlorides; and from 196° to 200°, nearly pure chloride of benzoyl, which is readily freed from traces of oxychloride by washing with water, and dried over chloride of calcium.—3. Sodic benzoate is treated in a similar manner with oxychloride of phosphorus: the reaction is violent even in the cold, and if the oxychloride be slightly in excess, chloride of benzoyl and sodic phosphate are the only products:

$$3C^7H^5NaO^2 + POCl^3 = 3C^7H^5O.Cl + PO^4Na^3,$$

otherwise benzoic anhydride is also formed. The distillate below 196° obtained in (2) may advantageously be employed for this purpose.

Chloride of benzoyl is a clear colourless liquid, with a peculiar smell, which resembles that of horse-radish and makes the eyes water. Specific gravity 1·196 (L. and W.); 1·25 at 15° C. (Cahours): boils at 196°: vapour-density (expt.) 4·987 (Cahours); 4·901 (calc.). It is insoluble in water, but is decomposed slowly by cold, and quickly by hot water, into benzoic and hydrochloric acid: the same decomposition is slowly effected when it is exposed to moist air. It is decomposed by alcohol, with evolution of heat, into benzoic ether and hydrochloric acid: it does not act upon pure ether. It is soluble in all proportions in bisulphide of carbon, without decomposition, and with the aid of heat dissolves sulphur and phosphorus, which crystallise out on cooling.

It burns with a bright, green-edged, very smoky flame. When boiled with *aqueous alkalis*, it is immediately decomposed into benzoate and chloride, but it may be distilled without alteration over anhydrous lime or baryta. With dry *ammonia* or *ammonic carbonate*, it forms benzamide and chloride of ammonium; it is similarly decomposed by phenylamine and other alkaloids, yielding phenylbenzamide, &c. It is decomposed by certain metallic *bromides*, *iodides*, *sulphides*, and *cyanides*, yielding bromide, iodide, sulphide, or cyanide of benzoyl. With *sulphocyanate of potassium*, it evolves heat, and yields carbonic anhydride and sulphide, and benzonitrile (Schiff, Ann. Ch. Pharm. xcix. 117): probably owing to the decomposition of sulphocyanate of benzoyl:

$$2(CNS.C^7H^5O) = 2C^7H^5N + CO^2 + CS^2 \text{ (Limpricht).}$$

It is not attacked by *potassium*. When heated with *hydride of copper*, it yields hydride of benzoyl and subchloride of copper (Chiozza). With *chloride of aluminium*, it forms a crystalline compound, but not with the chlorides of copper, magnesium, or zinc: it is decomposed by *perchloride of tin* (Casselmann). With the alkaline salts of many organic monobasic acids, it yields an alkaline chloride and an anhydride, *e. g.* with *sodic benzoate*, benzoic anhydride; with *sodic pelargonate*, benzopelargonic anhydride, &c. (Gerhardt). Heated with *formate of sodium*, it yields carbonic oxide, chloride of sodium, and benzoic acid:

$$CHNaO^2 + C^7H^5OCl = CO + NaCl + C^7H^6O^2 \text{ (Gerhardt).}$$

Heated with *potassic oxalate*, it yields benzoic anhydride, potassic chloride, and carbonic oxide and anhydride (Gerhardt) with *oxamide*, benzonitrile and other products (see BENZONITRIL), with most *amides*, a secondary or tertiary amide containing benzoyl.

When finely powdered *aldehyde-ammonia* is gradually added to chloride of benzoyl, sal-ammoniac and benzoic acid are formed, together with a substance which crystallises from hot alcohol in needles having the composition $C^{16}H^{16}N^2O^2$, isomeric (perhaps identical) with hipparaffin. It is insoluble in water, readily soluble in hot alcohol or ether; is fusible, and sublimes partly undecomposed; is slowly decomposed by boiling potash or sulphuric acid into benzoic acid and a brown resin; is not attacked by boiling with water and peroxide of lead, till sulphuric acid is added, when aldehyde is evolved and benzamide formed; is similarly decomposed by nitrous acid. (Limpricht, Ann. Ch. Pharm. xcix. 119.)

Pentachloride of phosphorus dissolves in hot chloride of benzoyl, and is deposited on cooling (Gerhardt). According to Schischkoff and Rosing (Compt. rend. xlvi. 867), when equivalent quantities of the two substances are heated together in a sealed tube to 200° C. for some days, a compound, $C^7H^5Cl^3$, is formed, which they call *perchloride of benzoyl*. The contents of the tube are heated in a retort to about 110° C., washed first with strong potash, and then with water, and dissolved in alcohol; the addition of water precipitates the compound as a yellowish neutral oil, heavier than water, soluble in alcohol or ether. It blackens at 130°—140°, and cannot be distilled without decomposition. It is decomposed when heated with water in a sealed tube, but not by mere contact with water or aqueous or solid potash: it is also decomposed by fuming nitric acid, evolving nitrous fumes; with acetate of silver in the cold it yields chloride of silver.

By the action of chlorine on benzoate of ethyl (*q. v.*) a compound is obtained, having the composition $C^{18}H^{16}Cl^6O^3$, which may be regarded as a compound of chloride of benzoyl with tetrachlorovinic ether, $C^{18}H^{16}Cl^6O^3 = 2C^7H^5OCl.C^4H^6Cl^4O$. It is a colourless liquid, boiling at 188°—190° C., of specific gravity 1·346 at 10·8°, smells like chloride of benzoyl, fumes in moist air, and is slowly decomposed by water into hydrochloric, benzoic, and acetic acids. (Malaguti, Ann. Ch. Phys. [2] lxx. 374.)

Chloride of benzoyl appears to form a compound with hydride of benzoyl. (See BENZOYL, HYDRIDE OF.)

Substitution-products of Chloride of Benzoyl.

Chloride of Chlorobenzoyl. $C^7H^4Cl^2O = C^7H^4ClO.Cl$. (Limpricht and v. Uslar, Ann. Ch. Pharm. cii. 262).—Obtained: 1. By the action of perchloride of phosphorus on chlorobenzoic acid.—2. By the decomposition of chlorosulphobenzoic acid:

$$C^7H^4Cl^2SO^3 = C^7H^4Cl^2O + SO^2.$$

1 at. sulphobenzoic acid is heated with 2 at. perchloride of phosphorus, as long as anything distils over; by repeated rectification of the distillate, a yellowish liquid is obtained, which boils at 285° C., and consists of impure chloride of chlorobenzoyl, which cannot be purified by distillation. As obtained by (1) it is a clear, colourless, strongly-refracting liquid, which boils at 225° C.: is slowly decomposed by boiling water into chlorobenzoic and hydrochloric acids, and quickly by strong aqueous ammonia, into chlorobenzamide and chloride of ammonium.

By the distillation of salicylic acid with perchloride of phosphorus Chiozza (Ann.

Ch. Phys. [3] xxxvi. 102) obtained a compound isomeric with the foregoing, which may be called *chloride of parachlorobenzoyl:*

$$C^7H^6O^3 + 2PCl^5 = C^7H^4Cl^2O + 2POCl^3 + 2HCl.$$

The distillate, which is probably not quite pure, is a heavy strongly-refracting liquid, with a suffocating smell, and decomposed slowly by cold, immediately by hot water, into parachlorobenzoic and hydrochloric acids: when gently heated with salicylous acid, it yields hydrochloric acid and salicylide of benzoyl. This reaction has not yet been explained.

Chloride of Nitrobenzoyl. $C^7H^4ClNO^3 = C^7H^4(NO^2)O.Cl.$ (Cahours (1848), Ann. Ch. Phys. [3] xxiii. 339; Bertagnini, *ibid.* [3] xxxiii. 465.)—Formed by the action of chlorine in the sunshine on hydride of nitrobenzoyl. Also by heating nitrobenzoic acid with perchloride of phosphorus; a mixture of the chlorides of phosphoryl and nitrobenzoyl distils over, which is rectified, and the portion which passes over last, is washed with water, dried over chloride of calcium, and again distilled. It is a yellow liquid, heavier than, and insoluble in, water, something like chloride of benzoyl, and boiling at 265°—268° C. It is gradually decomposed in moist air into nitrobenzoic and hydrochloric acids. It is similarly decomposed by strong boiling potash. With ammonia, it forms nitrobenzamide; with phenylamine, phenylnitrobenzamide. With alcohol or wood-spirit, it forms nitrobenzoate of ethyl or methyl: it is not decomposed by ether. F. T. C.

BENZOYL, CYANIDE OF. $C^8H^5NO = C^7H^5O.CN.$ (Liebig and Wöhler (1832), Ann. Ch. Pharm. iii. 267; H. Strecker, *ibid.* xc. 62.)—When chloride of benzoyl is distilled with cyanide of mercury, a yellow oil passes over, which may be obtained colourless by rectification (L. and W.); after a time, it solidifies to a crystalline mass, which, after washing with water as long as any mercury-salt is washed out, and drying with filter-paper and over sulphuric acid, leaves pure cyanide of benzoyl. It is a colourless crystalline body, which melts at 31° C., and crystallises by slow cooling in tables an inch long; it has a pungent odour, exciting tears; boils at 206°—208° C.; is heavier than water; is inflammable, and burns with a very smoky flame. It is very slowly decomposed by water in the cold, and not rapidly, even on heating: is decomposed by aqueous potash; also by ammonia, into benzamide and cyanide of ammonium; and by zinc and hydrochloric acid, into hydride of benzoyl and benzoin. F. T. C.

BENZOYL, HYDRIDE OF. *Benzaldine. Bitter-Almond Oil. Oxide of Picramyl. Oxide of Stilbene.* $C^7H^6O = C^7H^5O.H.$ (Liebig and Wöhler (1832), Ann. Ch. Pharm. xxii. 1.)—The principal constituent of crude bitter-almond oil, the volatile oil which is obtained by distilling bitter-almonds with water (see BITTER-ALMOND OIL). It is also formed by the decomposition of many organic substances. 1. By the oxidation of amygdalin, amygdalic acid, benzylic alcohol (Cannizzaro, Ann. Ch. Pharm. lxxxviii. 180), cinnamon-oil, cinnamic acid (Mulder, Dumas, and Péligot), and gum-benzoin, by nitric acid; of stilbene and styracene by aqueous chromic acid (Laurent); of mandelic acid, styrone, and (with several other products) of casein, albumin, fibrin, and gelatine, by sulphuric acid and binoxide of manganese.—2. By the action of hydride of copper on chloride of benzoyl (Chiozza, Compt. rend. xxxvi. 631).—3. By the rapid dry distillation of a mixture of benzoate and formate of calcium:

$$C^7H^5CaO^2 + CHCaO^2 = C^7H^6O + CO^3Ca^2$$

a brown oily liquid passes over, whence hydride of benzoyl is separated by acid sulphite of ammonium (Piria, Ann. Ch. Pharm. c. 104).—4. By the action of nascent hydrogen on cyanide of benzoyl. Cyanide of benzoyl is heated gently with hydrochloric acid and excess of zinc; the cyanide turns yellow, and the zinc becomes covered with an unctuous mass, containing hydride of benzoyl, hydrocyanic acid, and benzoin. This, when heated with potash, yields reddish-yellow oily drops, which, when distilled, yield pure hydride of benzoyl (Kolbe, Ann. Ch. Pharm. xcviii. 344).—5. By the action of oxalate of silver on chloride of benzylene,

$$C^7H^6Cl^2 + C^2Ag^2O^4 = C^7H^6O + CO^2 + CO + 2AgCl.$$

The mixture must be very cautiously heated under rock-oil, otherwise a violent reaction takes place, attended with complete destruction of the organic compound. (Golowkinsky, Ann. Ch. Pharm. cxi. 252.)

Crude bitter-almond oil contains, besides hydride of benzoyl, hydrocyanic and benzoic acids, benzoin, and benzimide. By submitting the oil to fractional distillation, hydrocyanic acid first passes over, and then tolerably pure hydride of benzoyl; the other compounds remain in the residue. Pure hydride of benzoyl may also be obtained from the crude oil by several chemical means: 1. By agitating the oil with powdered mercuric oxide and water (v. Ittner), or with milk of lime and protochloride of iron (W. and L.), and distilling.—2. By agitating the oil with three to four times its volume of acid sulphite of sodium of 27° B., or 1·231 specific gravity; drying by pressure, or on a porous tile, the crystalline mass which forms after some hours; washing it with cold alcohol; dissolving it in the smallest possible quantity of water, and decomposing it by a strong solution of sodic carbonate. The oil which separates is decanted and distilled over chloride of calcium (Bertagnini, Ann. Ch. Pharm. lxxxv. 186). According to Müller and Limpricht (Ann. Ch. Pharm. cxi. 136), it is necessary, in order to obtain a pure product by this method, either to recrystallise the crystalline compound before distilling it with carbonate of sodium, or to rectify the liquid which passes over; the portion which distils up to 184° C. is then free from hydrocyanic acid.

Pure hydride of benzoyl is a colourless, limpid, strongly-refracting liquid, with a smell resembling that of oil of bitter-almonds, and a burning aromatic taste. Its specific gravity is 1·0499 at 14·6 or 1·063 at 0° C. (Kopp); boils at 179·1° with the barometer at 751·3 mm.; vapour-density (calc.) 3·66. It is soluble in 30 pts. water, and in all proportions in alcohol and ether; when free from prussic acid, it is not poisonous; in the animal organism it is converted into hippuric acid (Wöhler and Frierichs, Ann. Ch. Pharm. lxvi. 336). It dissolves in sulphurous acid more easily than in water, and separates out on evaporating the solution. It is generally regarded as the aldehyde of the benzoic group, since it exhibits many of the reactions of an aldehyde, combining with acid sulphites of alkali-metals, and oxidising in moist air to benzoic acid; but it does not reduce silver-solutions.

It burns with a bright very smoky flame. It may be passed through a tube heated to dull redness without decomposition; but if the tube be filled with fragments of pumice-stone, it is decomposed into benzoyl and carbonic oxide (Barreswil and Boudault, J. Pharm. [3] v. 267). Heated to 100° C. in a sealed tube with ferric hydrate (previously dried at 100°) it is oxidised, and yields a considerable quantity of ferrous benzoate, part of the non-combined ferric oxide being also reduced to ferrous oxide (Gräger, Ann. Ch. Pharm. cxi. 124). Dry *chlorine* converts it into chloride of benzoyl and hydrochloric acid; this decomposition is seldom complete, especially if the gas be moist, a compound of chloride and hydride of benzoyl being formed (see below). *Bromine* converts it into bromide of benzoyl and hydrobromic acid. *Iodine* does not attack it. Cold strong *nitric acid* dissolves it undecomposed, and on heating, slowly oxidises it into benzoic acid: fuming nitric acid, or nitrosulphuric acid, converts it into hydride of nitrobenzoyl (see below). Strong *sulphuric acid* dissolves it, forming a red solution, which blackens and gives off sulphurous anhydride when heated. With *sulphuric anhydride* it forms a sulpho-conjugated acid, sulphomandelic acid (Mitscherlich, Lehrb. 4te Aufl. i. 163). With *perchloride of phosphorus*, it yields the chlorides of benzylene and phosphoryl (Cahours, Compt. rend. xxv. 725). Heated with *chloride of acetyl* in equivalent proportions for several hours to 120°—130° C. in a sealed tube, it yields hydrochloric and cinnamic acids (Bertagnini, Ann. Ch. Pharm. c. 125):

$$C^7H^6O + C^2H^3O.Cl = C^9H^8O^2 + HCl.$$

With *sulphydric acid* or *sulphide of ammonium*, it yields peculiar products containing sulphur, and varying according to the amount of alkali present, and the medium in which the hydride of benzoyl is dissolved. In an alcoholic solution, it yields hydride of thiobenzoyl (see below); in an ethereal solution, *thiobenzaldine*. With *ammonia* and *sulphide of carbon* it yields *sulphocyanobenzylene*. It dissolves *potassium*, becoming thick and dark, but without evolution of hydrogen (Löwig). When heated with solid *potash*, it evolves hydrogen, and is converted into benzoate; with alcoholic potash, into benzoate and benzylic alcohol. *Cyanide of potassium* converts it into benzoin. With *ammonia* it forms various products (Laurent); with *aqueous* ammonia hydrobenzamide and azobenzoilide; with *alcoholic* ammonia amarine, benzimic-acid, and sometimes, dibenzoylimide (Robson). With *aniline*, it yields benzylene-phenylamine; with *urea*, benzoyluride.

Combinations. Benzoate of Hydride of Benzoyl. See BITTER-ALMOND OIL. *Hydride of Benzoyl with Chloride of Benzoyl.* $C^{14}H^{11}ClO^2 = C^7H^6O.C^7H^5OCl$ (Laurent and Gerhardt, Compt. chim. 1850, p. 123.)—Formed abundantly when hydride of benzoyl is imperfectly saturated with chlorine, or even when it is treated with excess of chlorine. The saturated solution, when left to itself in a stoppered bottle, gradually solidifies into a crystalline mass, which is washed with cold alcohol, and dried. It forms colourless shining laminæ, resembling benzoic acid; melts very readily, and remains liquid a long time when at rest; heated above its melting point it gives off chloride of benzoyl. When dry, it is inodorous, but if moist it gives off fumes of hydrochloric acid, and smells of hydride of benzoyl. Hot water decomposes it into benzoic and hydrochloric acids, and hydride of benzoyl. It is insoluble in cold alcohol; warm alcohol decomposes it. It is decomposed by strong sulphuric acid.

Hydrocyanate of Hydride of Benzoyl. $C^8H^7NO = C^7H^6O.CNH$ (**Voelckel** (1844), Pogg. Ann. lxii. 444).—When crude bitter-almond oil or bitter-almond water is mixed with hydrochloric acid, and evaporated below 100° C., till it is considerably concentrated, this compound separates as a yellowish oil, which is washed with water, and dried over sulphuric acid in vacuo. It is inodorous; boils at 170° C. Specific gravity 1·24. Slightly soluble in water, forming a bitter or neutral solution, readily in alcohol or ether. It begins to decompose at 100° C., and when boiled is entirely resolved into hydride of benzoyl and hydrocyanic acid; it is similarly decomposed by aqueous potash. When evaporated with strong hydrochloric acid, it takes up water and forms mandelic acid and ammonia:

$$C^8H^7NO + 2H^2O = C^8H^8O^3 + NH^3.$$

Gerhardt (Traité, iii. 193) mentions a compound obtained by distilling in a brine-bath, a mixture of 2 pts. hydride of benzoyl, 1 pt. cyanide of mercury, and 1 pt. hydrochloric acid; it is an oil which smells like hydride of benzoyl, has a specific gravity of 1·10; is somewhat soluble in water, more in alcohol, readily in ether; does not solidify at 12° C.; boils at 312°, yielding a distillate which crystallises on cooling.

Hydride of Benzoyl with Chloride of Calcium.—When dry pulverised chloride of calcium is added to anhydrous bitter-almond oil, heat is evolved, and a solid compound is formed, which separates from the liquid in easily decomposible crystals, apparently containing 2·5 to 3·3 at. CaCl to 1 at. hydride of benzoyl. (**Ekmann**, Ann. Ch. Pharm. cxii. 151.)

Hydride of Benzoyl with Acid Sulphites of Alkali-metals. (**Bertagnini**, Ann. Ch. Pharm. lxxxv. 183.)

a. With Acid Sulphite of Ammonium.—Hydride of benzoyl dissolves in all proportions in acid sulphite of ammonium; but the resulting compound cannot be obtained in the crystalline state. The solution dissolves an excess of hydride of benzoyl, which separates out on addition of water. Ammonia renders it turbid, and gradually precipitates a body having the properties of hydrobenzamide. When the dry compound is heated with excess of slaked lime, it yields amarine and lophine. (**Gössmann.**)

b. With Acid Sulphite of Potassium.—When hydride of benzoyl is shaken up with a solution of this salt of 28°—30° Baumé (specific gravity 1·24—1·26), a crystalline magma is speedily formed, which must be dried with filter-paper, and dissolved in dilute boiling alcohol (if boiled too long decomposition takes place); the solution on cooling deposits the compound in shining rectangular laminæ. It is very soluble in water, less so in presence of alkaline sulphites, not at all in a saturated solution of these salts; sparingly soluble in cold, readily in boiling, alcohol. It is permanent in the air. Its aqueous solution is decomposed by boiling, either alone or with dilute acids, and by alkaline carbonates, with separation of hydride of benzoyl.

c. With Acid Sulphite of Sodium. $C^7H^6O.SO^3NaH. \frac{1}{2}Aq.$—Formed like (*b*). Small white aggregated prisms, tasting of hydride of benzoyl and sulphurous acid, readily soluble in water, sparingly in hot alcohol, insoluble in cold alcohol. It may be kept in stoppered bottles, and decomposes but slowly when exposed to the air. When carefully heated in the air, it is decomposed without blackening, into sulphurous anhydride and hydride of benzoyl, sulphite of sodium remaining; in a stream of hydrogen, this decomposition takes place below 100° C. Its aqueous solution is decomposed by boiling, either alone or with acids or alkalis, like that of (*b*), also by iodine or chlorine, sodic sulphate being formed. Nitric acid decomposes the dry salt in a similar manner. Its aqueous solution gives, with barium-salts, a white precipitate, soluble in hydrochloric acid; it also precipitates lead- and silver-salts: the precipitates appear to contain a portion of the oil.

Substitution-products of Hydride of Benzoyl.

Hydride of Nitrobenzoyl. Nitrobenzaldide. $C^7H^5NO^3 = C^7H^4(NO)^2O.H$ (**Bertagnini**, Ann. Ch. Pharm. lxxix. 259; lxxxvi. 190.)—When hydride of benzoyl is gradually added to fuming nitric acid, or to 15—20 vols. of a mixture of 1 vol. nitric and 2 vols. sulphuric acid, heat is evolved, and the addition of water precipitates hydride of nitrobenzoyl in yellowish oily drops, which crystallise in a few days. The vessel must be kept cool during the operation, otherwise nitrobenzoic acid will be formed. The crystals are contaminated by a yellow fetid oil, whence they are purified by pressure between filter-paper, and recrystallisation from boiling dilute alcohol.

It forms white shining needles, inodorous when pure, with a taste like that of hydride of benzoyl. It is slightly soluble in cold, readily in hot water or alcohol, less so in ether; dissolves undecomposed in nitric, hydrochloric, or sulphuric acids, and crystallises out as the last solution absorbs moisture from the air. It melts easily to a colourless liquid, which solidifies at 46° C.; when further heated, it gives off vapours, which smell pleasantly when dilute, but are very pungent when concentrated. It may be volatilised in small quantities without decomposition; partly even when boiled with water, completely when heated in an oil-bath in a stream of gas.

Hydride of nitrobenzoyl burns with a smoky flame. It does not absorb oxygen from the air, but is readily converted into nitrobenzoic acid by oxidising agents, *e. g.* aqueous chromic acid, or a mixture of nitric and sulphuric acids. *Chlorine* in sunshine converts it into *chlorine of nitrobenzoyl* (see BENZOYL, CHLORIDE OF). *Bromine* dissolves readily in fused hydride of nitrobenzoyl, but does not decompose it till heated over 100° C., when a brown resinous mass is formed. Strong *hydrocyanic acid* readily dissolves it, the solution, if evaporated at once, deposits it unaltered, but after standing for a few hours, yields on evaporation, a viscid liquid, permanent in the air, soluble in hot water, and separating out on cooling, which, when boiled with hydrochloric acid, yields chloride of ammonium, and another body soluble in water. *Cyanide of potassium* decomposes it at once, forming compounds which have not been examined. With *sulphydric acid*, its alcoholic solution forms *hydride of thionitrobenzylene* (see below). When its solution in alcoholic ammonia is treated with sulphuretted hydrogen, a semifluid mass is deposited, which consists of a sulphur-compound mixed with free sulphur; the former is dissolved out by ether, and obtained by evaporation as a viscid reddish liquid, insoluble in water or dilute acids, soluble in warm alcohol; it is decomposed by heat, evolving sulphuretted hydrogen, and when boiled with nitric acid, forms sulphuric acid and a yellow resin. Heated with *sulphite of ammonium* it yields an acid product, readily soluble in water or alcohol. *Alcoholic potash* converts it into nitrobenzoate in the cold; *aqueous potash* requires the aid of heat. *Ammonia*, whether dry, aqueous, or alcoholic, converts it into trinitrohydrobenzamide. When it is gently heated with *urea*, water is given off, and the whole solidifies on cooling into an opaque mass (nitrobenzoylureid?) slightly soluble in alcohol, readily in alcohol containing hydrochloric acid, being thereby decomposed into urea and hydride of nitrobenzoyl.

Hydride of nitrobenzoyl combines with acid sulphites of alkali-metals, forming compounds of which the following have been examined:

a. With Acid Sulphite of Ammonium. $C^7H^5NO^3.SO^3NH^5 + \frac{1}{2}\,Aq.$—Hydride of nitrobenzoyl is dissolved in a solution of acid sulphite of ammonium of 29° Bm. at a gentle heat, when this compound crystallises out on cooling. It forms small, transparent, colourless prisms, which grate between the teeth, and have a bitter and sulphurous taste; are soluble in water or boiling alcohol, and crystallise readily from the latter solution only. It is permanent in the air, though it gradually acquires a violet tinge. Its aqueous solution is decomposed by boiling, either alone or with acids or alkalis. With barium- lead- or silver-salts, its aqueous solution gives a precipitate of metallic sulphite mixed with hydride of nitrobenzoyl; with dichloride of platinum, it gives chloroplatinate of ammonium.

b. With Acid Sulphite of Sodium. $C^7H^5NO^3.SO^3NaH + 5Aq.$—Obtained in the same manner manner as (*a*), in yellow scales, which are rendered nearly colourless by recrystallisation from a little hot water. It is readily soluble in hot, less so in cold water: effloresces in the air: loses its water at 70°—80° C.; above 90° it is decomposed giving off hydrogen, sulphurous anhydride, and hydride of nitrobenzoyl, sulphite of sodium remaining behind. Its aqueous solution is decomposed by boiling, especially on addition of acids or alkalis.

Hydride of Thiobenzoyl. Hydride of Sulphobenzoyl. Sulphide of Stilbene. Sulphopicramyl. $C^7H^6S = C^7H^5S.H$ (Laurent, Ann. Ch. Phys. [3] i. 292. Rochleder, Ann. Ch. Pharm. xxxvii. 346. Cahours, Compt. rend. xxv. 357.)—When 1 vol. of bitter-almond oil (crude or pure), is dissolved in 8—10 vols. alcohol, and 1 vol. sulphide of ammonium gradually added, this compound speedily separates as a mealy powder, which is easily purified by washing with alcohol. It is also obtained when an alcoholic solution of hydrobrobenzamide is supersaturated with sulphuretted hydrogen, and the liquid left at rest. It is a white powder consisting of microscopic granules; is inodorous, but imparts to the fingers a smell of onions; is insoluble in water or alcohol. With ether it forms a transparent liquid, which resolidifies on adding a few drops of alcohol. It becomes soft at 90°—95° C. After fusion it solidifies to a transparent non-crystalline mass. By dry distillation, it evolves sulphuretted hydrogen and bisulphide of carbon, and yields a sublimate of stilbene and thionessal:

$$8C^7H^6S = 2CS^2 + 3H^2S + \underset{\text{Stilbene.}}{2C^{14}H^{12}} + \underset{\text{Thionessal.}}{C^{26}H^{18}S.}$$

It burns with an offensive smell and bright smoky flame. With *bromine*, it evolves hydrobromic acid, and forms an oily body. Heated with *nitric acid*, it yields sulphuric acid and hydride or hydrate of benzoyl; with *sulphuric acid*, it dissolves, forming a carmine solution, which water decolorises, precipitating yellow flakes; boiled with *hydrochloric acid*, it evolves a little sulphuretted hydrogen. It is slowly decomposed by *alcoholic potash;* water separates an oil from the solution, and acids evolve sulphuretted hydrogen from the alkaline liquid. It is isomeric with sulphide of benzylene.

Hydride of Thionitrobenzoyl. Sulphide of Nitrobenzylene. $C^7H^5NO^2S = C^7H^4(NO^2)S.H$ (Bertagnini, Ann. Ch. Pharm. lxxix. 269).—When an alcoholic solution of hydride of nitrobenzoyl is saturated with sulphuretted hydrogen, this compound separates as a grey light mealy powder, which is inodorous, but imparts a disagreeable smell to the fingers. It becomes electric when rubbed. It does not dissolve in the usual solvents, but melts in boiling *water*, aggregates together in boiling *alcohol*, and becomes soft and transparent with *ether* in the cold. It dissolves in strong *sulphuric acid*, and is reprecipitated unaltered by water. Strong nitric acid decomposes it in the cold, dilute *nitric acid* on heating, forming sulphuric acid and hydride of nitrobenzoyl. *Alcoholic potash* dissolves it in the cold, and water precipitates a brown substance from the solution. *Ammonia*, whether dry or aqueous, attacks it, evolving sulphuretted hydrogen, and forming (probably) trinitrohydrobenzamide.

Oxyiodide of Benzaldide. $C^{21}H^{18}I^4O$ (Geuther and Cartmell, Ann. Ch. Pharm. cxii. 1).—This compound, which may be regarded as a triple molecule of hydride of benzoyl ($C^{21}H^{18}O^3$), having 2 at. O replaced by 4 at. I, is produced by the action of hydriodic acid gas on hydride of benzoyl. Two layers of liquid are thereby formed, the upper consisting of aqueous hydriodic acid; the lower, which is oily, of the oxyiodide: the latter may be purified by repeated treatment with water and acid sulphite of sodium. It is then obtained as a solid mass, which melts at 28° C. and crystallises at 25° in colourless rhombic plates; smells like cress; dissolves readily in alcohol and ether, and is insoluble in water. It may be distilled with water without decomposition; is not decomposed by acid sulphites of alkali-metals, but is resolved by alcoholic potash into iodide of potassium, a small quantity of benzoic acid, and an oily body soluble in alcohol, but different from bitter-almond oil. By ammonia, it appears to be gradually converted into hydride of benzoyl. Boiled with nitrate of silver, it forms iodide of silver, and emits an odour of bitter-almond oil. F. T. C.

BENZOYL, IODIDE OF. $C^7H^5O.I.$ (Liebig and Wöhler, Ann. Ch. Pharm. iii. 266.)—Obtained readily by heating iodide of potassium with chloride of benzoyl; a brown liquid distils over, which solidifies to a crystalline mass, coloured brown by free iodine. When pure, it is colourless, lamino-crystalline and readily fusible, always with partial decomposition; in solubility and general reactions it resembles bromide of benzoyl. F. T. C.

BENZOYL, PERCHLORIDE OF. See BENZOYL, CHLORIDE OF.

BENZOYL, SULPHIDE OF. $(C^7H^5O)^2S$ (Liebig and Wohler, *loc. cit.*)—When chloride of benzoyl is distilled with finely-powdered sulphide of lead, a yellow oil passes over, which solidifies to a soft yellow crystalline mass. It has an unpleasant sulphurous smell; is not decomposed by boiling with water or alcohol, and but slowly with aqueous potash; burns with a bright smoky flame, giving off sulphurous anhydride. F. T. C.

BENZOYL SULPHOCYANIDE OF. See SULPHOCYANOBENZYLENE.

BENZOYLAZOTIDE. $C^{15}N^2H^{12}$ (Laurent (1837), Ann. Ch. Phys. [2] lxvi. 187. Laurent and Gerhardt, Compt. chim. (1850), 115. Robson, Chem. Soc. Qu. J. iv. 225).—A product of the action of ammonia on bitter-almond oil. It is the residue insoluble in alcohol, obtained in the preparation of *azobenzoyl*, *benzhydramide*, and *dibenzoylimide* (*q. v.*) It is a white powder, without taste or smell, consisting of microscopic prisms. It is insoluble in water; requires 300—400 pts. boiling alcohol for its solution, and at least as much ether. Fuses when heated, and solidifies to a vitreous mass, in which a few oblique prisms separate. When boiled with alcohol and hydrochloric acid, it is slowly decomposed, evolving hydrocyanic acid. By dry distillation, it yields an oil, then a sublimate of lophine and amarone, and finally a carbonaceous residue.

Gerhardt (Traité, iii. 194) describes this body and benzhydramide under the name of *hydrides of cyanazobenzoyl*.

Quadrat (Ann. Ch. Pharm. lxxi. 18), by heating sulphocyanobenzylene, obtained a resinous mass, which, when exhausted with alcohol, left a crystalline residue, insoluble in water, almost so in alcohol, to which he assigns the formula $C^{15}H^{10}N^2$. The crystals are permanent at 100° C. and are not decomposed by nitric acid. F. T. C.

BENZOYL-BENZOIN. See BENZOIN.

BENZOYL-UREA. Syn. with BENZOCARBAMIDE. See CARBAMIDE.

BENZOYLUREID. $C^{25}H^{28}N^{8}O^{4}$ (Laurent and Gerhardt, Compt. chim. [1850], p. 119).—Formed by the action of urea on hydride of benzoyl:

$$4CH^{4}N^{2}O + 3C^{7}H^{6}O = C^{25}H^{28}N^{8}O^{4} + 3H^{2}O.$$

When 5 pts. powdered urea are heated to somewhat below 100° C. with 2 pts. hydride of benzoyl, the mixture becomes liquid, and shortly solidifies to a compact mass. When cold, this is powdered, freed from excess of hydride of benzoyl by ether, and of urea by boiling with water; the residue, which is dried at 120°, is benzoylureid. It is a white amorphous powder, without smell or taste, insoluble in water or ether, soluble in alcohol, whence it separates on evaporation in amorphous crusts. It turns yellow at 170° C. gives off hydride of benzoyl a few degrees higher, and when further heated, yields hydride of benzoyl and ammoniacal water, leaving a yellow residue, which finally volatilises completely, and is sparingly soluble in alcohol. When boiled with dilute acids, it is decomposed into hydride of benzoyl and urea. It is not decomposed by boiling ammonia; slowly by strong boiling potash, evolving ammonia and hydride of benzoyl, and leaving potassic benzoate in solution. Hydride of nitrobenzoyl yields with urea a similar compound. (Bertagnini.) F. T. C.

BENZUREID. Syn. with Benzoyl-urea. See Carbamide.

BENZYL. *Tolyl. Toluenyl.* $C^{7}H^{7}$.—A hypothetical radicle, isomeric with cresyl, contained in benzylic alcohol, toluene, and other compounds. F. T. C.

BENZYL, CHLORIDE OF. *Chloride of Tolyl* or *Toluenyl. Chlorotoluol.* $C^{7}H^{7}Cl$ (Cannizzaro, Ann. Ch. Pharm. lxvxviii. 129; xcvii. 246. Deville, Ann. Ch. Phys. [3] iii. 178).—Obtained by saturating benzylic alcohol with hydrochloric acid gas whereupon heat is evolved, and the liquid divides itself into two layers, the lower of which is aqueous hydrochloric acid, the upper chloride of benzyl. Or by passing chlorine into hydride of benzyl in the dark, expelling excess of chlorine by a stream of carbonic anhydride, and rectifying the product. It forms a colourless liquid, of specific gravity 1·117 at 0° C; boils at 170° (Deville); 175°—176° (Cannizzaro); insoluble in water, soluble in alcohol or ether. It is not attacked by aqueous potash; alcoholic potash decomposes it on boiling into benzylethylic ether and chloride of potassium. When boiled with an alcoholic solution of acetate of potassium, it is converted into acetate of benzyl; of cyanide of potassium, into cyanide of benzyl. When heated in a sealed tube with alcoholic ammonia, it yields tribenzylamine. F. T. C.

BENZYL, CYANIDE OF. *Cyanide of Tolyl* or *Toluenyl.* $C^{8}H^{7}N = C^{7}H^{7}.CN$ (Cannizzaro, Ann. Ch. Phys. [3] xlv. 468).—Obtained by boiling chloride of benzyl with a strong alcoholic solution of cyanide of potassium, till no more chloride of potassium separates out, and distilling the filtrate to remove the alcohol. The residual liquid separates into two layers, the upper containing cyanide of benzyl, which may be obtained from it by rectification. It is a colourless liquid, which, by boiling with strong potash, is converted into toluic acid, $C^{8}H^{8}O^{2}$. F. T. C.

BENZYL, HYDRATE OF. Syn. with Benzylic Alcohol (*q. v.*)

BENZYL, HYDRIDE OF. *Hydride of Tolyl* or *Toluenyl. Toluene* or *Toluol. Benzoene. Dracyl.* $C^{7}H^{8} = C^{7}H^{7}.H$.—Discovered by Pelletier and Walter (1837) in the oily products obtained in the manufacture of illuminating gas from resin; first examined by Deville.

Formed: 1. By the action of potash on benzylic alcohol (Cannizzaro, Ann. Ch. Pharm. xc. 252; xcvi. 246):

$$3C^{7}H^{8}O + KHO = C^{7}H^{5}KO^{2} + 2C^{7}H^{8} + 2H^{2}O.$$

2. By heating toluic acid with excess of lime (Noad, *ibid.* lxiii. 305):

$$C^{8}H^{8}O^{2} = C^{7}H^{8} + CO^{2}.$$

3. By the dry distillation of tolu-balsam (Deville, Ann. Ch. Phys. [3] iii. 152, 168; Muspratt and Hofmann, Ann. Ch. Pharm. liv. 9); of dragon's blood (Glénard and Boudault, Ann. Ch. Phys. [3] iv. 274); of the resin of *Pinus maritima* (Pelletier and Walter, *ibid.* [2] lxvii. 269); of Burmese naphtha (De la Rue and Müller, Proc. Roy. Soc. viii. 221); of resin-oil (Couerbe, Ann. Ch. Phys. [2] lxix. 184); of wood (Völckel, Ann. Ch. Pharm. lxxxvi. 334), and of coal. In distilling coal-tar, the portion which passes over at 100°—115° C. consists of toluene (Mansfield, Chem. Soc. Qu. J. i. 266).—4. The yellow oil which separates from crude wood-spirit on addition of water contains hydride of benzyl. (Cahours, Compt. rend. xxx. 319.)

Preparation.—1. When benzylic alcohol is distilled with four or five times its volume of strong alcoholic potash in an apparatus which allows the less volatile products to run back again, alcohol first passes over, then water, and finally, when the residue has become solid, a mixture of hydride and hydrate of benzyl. This mixture is distilled by itself, the portion which passes over at 116° C. collected apart and shaken up with sulphuric acid, the decanted liquid washed with potassic carbonate, and twice rectified over phosphoric anhydride.—2. When tolu-balsam, freed by distillation with water from toluene, cinnamein, and a portion of the benzoic acid is subjected to dry distillation, there passes over,—besides carbonic oxide and anhydride,—water, abundance of benzoic, and a little cinnamic acid, a heavy oil consisting of a mixture of benzoate of ethyl (benzoate of methyl, according to Muspratt and Scharling), and hydride of benzyl. This oil is distilled, and the portion which passes over at 13°—140° C. repeatedly rectified over strong aqueous potash, and dried over chloride of calcium. E. Kopp (Compt. chim. 1849, p. 149) purifies the balsam by boiling with sodic carbonate, boils the residue with strong aqueous soda, distils the brown solution, decants the oil which passes over from the water which accompanies it, and rectifies it repeatedly.—3. To prepare hydride of benzyl from coal-tar, the oil which comes over at 100°—120° C. is mixed with half its weight of sulphuric acid and rectified, when a product of constant boiling-point is obtained. (Wilson, Chem. Soc. Qu. J. iii. 154.)

Hydride of benzyl is a colourless, very mobile, strongly refracting liquid, with a smell like benzene, and a burning taste; specific gravity 0·87 at 18° C. (Deville). The boiling-point is variously stated at from 103°·7 (Church), to 114° (Gerhardt), vapour-density 3·27 (Deville); does not solidify at −20°. It is insoluble in water, slightly soluble in alcohol, more so in ether or in fixed or volatile oils. It dissolves most resins, also iodine, forming an amber-red solution, and, when heated, sulphur, which crystallises out on cooling.

It is not decomposed when passed through a red-hot tube filled with potash-lime. It burns with a smoky flame. With *chlorine*, it evolves heat, and yields several substitution-compounds (see below). With fuming *nitric acid*, it yields substitution-compounds (see below). It dissolves in fuming *sulphuric acid*, forming sulphibenzylic (sulphotoluic) acid, and sulphibenzyl (sulphotoluol). It is not attacked either by *potassium* or by *potash*. When digested with *sodium*, in a closed vessel for fourteen days, it yields two substances, boiling respectively at 97° C. and 112°. (Church, Phil. Mag. [4] ix. 256.)

Substitution-products of Hydride of Benzyl.

Deville (Ann. Ch. Phys. [3] iii. 178) enumerates several compounds obtained by the action of chlorine on hydride of benzyl. When the reaction takes place in the dark, *chloride of benzyl* (chlorotoluol) is the product (see BENZYL, CHLORIDE OF). When chlorine is passed through hydride of benzil in bright daylight, as long as hydrochloric acid is evolved, and excess of chlorine removed by carbonic anhydride, *hydrochlorate of trichlorotoluol*, $C^7H^4Cl^6 = C^7H^5Cl^3.HCl$, is formed; when distilled it decomposes and evolves hydrochloric acid. When the action of the gas is still further prolonged, a thickish liquid is formed, together with some crystals. If the liquid be separated, further treated with chlorine with aid of heat, and purified by carbonic anhydride, the product is *dihydrochlorate of pentachlorotoluol*, $C^7H^5Cl^7 = C^7H^3Cl^5.2HCl$; when distilled it evolves hydrochloric acid; it is soluble in ether. The crystals are *trihydrochlorate of pentachlorotoluol*, $C^7H^6Cl^8 = C^7H^3Cl^5.3HCl$, they are purified by recrystallisation from ether, in which they are soluble, especially with aid of heat; they are colourless when pure. When the liquid and crystals together are distilled in a stream of chlorine, the distillate being repeatedly poured back again, the whole is gradually converted into a silky substance, abundance of hydrochloric acid being evolved; this substance, which is *hexchlorotoluol* (hydride of hexchlorobenzyl), $C^7H^2Cl^6$, is purified by pressure between filter-paper and recrystallisation from ether; it is volatile without decomposition.

Hydride of Nitrobenzyl. *Nitrotoluol.* $C^7H^7NO^2 = C^7H^6NO^2.H$. (Deville, *loc. cit.;* Glénard and Boudault, Compt. rend. xix. 505; Hofmann and Muspratt, Ann. Ch. Pharm. liii. 220, 224.)—Hydride of benzyl is added to cold fuming nitric acid as long as it dissolves immediately; on adding water to the red solution, hydride of nitrobenzyl separates as a red liquid, which may be decolorised by washing with water and repeated distillation. It is a nearly colourless liquid, smelling of bitter almonds, with a very sweet and afterwards pungent taste; specific gravity 1·18 at 16°·5 C.; vapour-density 4·95; boils at 225°—230° C. Readily soluble in alcohol or ether. It is partially decomposed by distillation, completely when passed at a high temperature through a red-hot tube filled with pieces of glass. It burns with a smoky flame, emitting the odour of gum-benzoin; when passed over red-hot baryta, it is resolved into phenylamine and carbonic anhydride. With fuming sulphuric acid it forms nitrosulphotoluic acid (Church). Aqueous potash dissolves it, forming a red solution, whence hydrochloric acid precipitates a brown powder; with alcoholic potash it forms a black liquid, whence a reddish oil containing phenylamine is obtained by distillation. Boiled with alcoholic sulphite of ammonium, it forms thiotoluate of ammonium. With sulphide of ammonium, it yields benzylamine.

Hydride of Dinitrobenzyl. *Dinitrotoluol.* $C^7H^6N^2O^4 = C^7H^5(NO^2).^2H$. (Deville, *loc. cit.*; Cahours, Compt. rend. xxiv. 555.)—Obtained by boiling hydride of benzyl with fuming nitric acid, or treating it with nitrosulphuric acid. It crystallises from alcohol in lustrous, hard, brittle, prismatic needles, which melt at 71° C. and solidify to a radiated mass. It boils at 300°, becoming coloured, and leaving a residue: when strongly heated, it yields a sublimate. It is sparingly soluble in water. It is not attacked by fuming nitric acid. Its solution in potash deposits a brown powder on addition of hydrochloric acid. Sulphide of ammonium converts it into nitrobenzylamine. F. T. C.

BENZYL, IODIDE OF. C^7H^7I. (Cannizzaro, 1854.)—When a solution of benzylic alcohol in bisulphide of carbon is mixed with a solution of phosphorus in bisulphide of carbon, iodine gradually added, and excess of bisulphide distilled off, a liquid is obtained, which irritates the eyes, and is probably iodide of benzyl.

F. T. C.

BENZYLAMINE. *Toluidine.* $C^7H^9N = N.C^7H^7.H^2$. (Muspratt and Hofmann (1845), Ann. Ch. Pharm. liv. 1; Noad, *ibid.* lxiii. 305; Hofmann, *ibid.* lxvi. 144; Wilson, Chem. Soc. Qu. J. iii. 154; Chautard, J. Pharm. [3] xxiv. 166.)—Formed by the reduction of hydride of nitrobenzyl by sulphydric acid (Muspratt and Hofmann): or by the action of potash on the yellow resin obtained by treating oil of turpentine by nitric acid. (Chautard.)

Preparation.—1. A solution of hydride of nitrobenzyl in alcohol saturated with ammonia, is treated with sulphuretted hydrogen till it smells strongly of the gas, even after long standing: sulphur then crystallises out. The reaction is accelerated by the application of heat, but the decomposition is never complete. The product is mixed with water and hydrochloric acid, and shaken up with ether to remove undecomposed hydride; it is then evaporated to $\frac{1}{3}$, and distilled with potash, when water, ammonia, and benzylamine pass over, the last as a heavy oil, which soon crystallises. The whole distillate is saturated with oxalic acid, evaporated to dryness on the water-bath, and exhausted with boiling absolute alcohol, which dissolves only the oxalate of benzylamine, which crystallises on cooling. The crystals are washed, dissolved in boiling water, and the solution decomposed by strong potash, when benzylamine separates in oily drops, which collect and crystallise into a radiated mass on cooling: it is purified by washing and one rectification, or by crystallisation from ether.—2. The resin obtained by treating oil of turpentine with nitric acid, is gradually mixed with aqueous potash; the mixture assumes a dark-brown colour, and becomes hot, and when the reaction has ceased, it is distilled as long as alkaline vapours pass over. The distillate is supersaturated with hydrochloric acid, evaporated to dryness over the water-bath, and exhausted with absolute alcohol, which dissolves hydrochlorate of benzylamine, and leaves sal-ammoniac undissolved.

Benzylamine crystallises from dilute alcohol in large colourless laminæ, which are sparingly soluble in cold, more readily in boiling, water: readily in alcohol, ether, wood-spirit, acetone, fixed and volatile oils, and bisulphide of carbon. It smells like phenylamine, and has a burning taste. It evaporates at ordinary temperatures, melts at 40° C. to a colourless, strongly-refracting oil, and boils at 198°. It is heavier than water; slightly blues red litmus, but does not redden turmeric; colours fir-wood deep yellow, but does not give the purple colour of phenylamine with chloride of lime, but only a faint reddish tint. With nitric acid benzylamine gives a deep-red, phenylamine a deep-blue, colour.

Bromine acts on benzylamine violently: when the product is heated, shining needles sublime, insoluble in water, soluble in alcohol and ether,—probably *tribromobenzylamine.* It is decomposed by boiling with strong *nitric acid,* with evolution of nitrous fumes; water added to the solution precipitates yellow flakes, which dissolve in alkalis, and are reprecipitated by acids. With aqueous *chromic acid,* it gives a red-brown precipitate. When its vapour is passed over fused *potassium,* vivid combustion takes place, and potassic cyanide is formed. *Cyanogen* passed into its alcoholic solution, yields cyanobenzylamine (see below).—With *chloride of cyanogen* it forms melobenzylamine (metoluidine) (see below.) With *bromide* or *iodide of ethyl,* it yields benzylethylamine (see below).

Combinations. 1. With Acids.—Benzylamine combines with acids, forming crystalline salts, which are mostly inodorous and colourless, but quickly become rose-coloured when exposed to the air: they are decomposed by alkalis or alkaline carbonates, benzylamine being separated as a crystalline curd. The *chloraurate,* $AuCl^4C^7H^{10}N$, separates as a thick precipitate, which soon aggregates to a crystalline mass, when the hydrochlorate is mixed with trichloride of gold: it melts in water at 50° — 60°C., dissolves when further heated, and crystallises on cooling in fine yellow needles. The *chloroplatinate,* $PtCl^3C^7H^{10}N$, separates as an orange-yellow crystalline pulp, when the hydrochlorate is mixed with bichloride of platinum: it is washed with ether-alcohol and dried in a water-bath. The *chloropalladate* is similar in appearance. The *hydrochlorate*, $C^7H^{10}NCl$, is deposited in white crystalline scales, becoming yellow on exposure to the air, when a solution of benzylamine in hydrochloric acid is evaporated and cooled: it is readily soluble in water or alcohol, sparingly in ether, forming acid solutions: when gently heated, it sublimes like sal-ammoniac. The *nitrate*, *phosphate*, and *sulphite* are crystallisable. The *acid oxalate*, $C^2O^4.C^7H^{10}N.H + \frac{1}{2}Aq$, is obtained by mixing an alcoholic solution of benzylamine with excess of oxalic acid, in delicate silky needles, soluble in boiling water or alcohol, insoluble in ether. The *sulphate*, $SO^4(C^7H^{10}N)^2$, is obtained when a few drops of sulphuric acid are added to an ethereal solution of benzylamine, as a white crystalline precipitate, which may be washed with ether: it is readily soluble in water, sparingly in alcohol. With *cupric sulphate* or *chloride*, benzylamine gives a greenish crystalline precipitate; with *nitrate of silver*, a white precipitate, which soon blackens; it precipitates ferric hydrate from ferric chloride.

2. With CYANOGEN; *Cyanobenzylamine; Cyanotoluidine.* $C^8H^8N^2 = C^7H^8N.CN$. (Hofmann, *loc. cit.* Chem. Soc. Qu. J. i. 170.)—When cyanogen is passed through an alcoholic solution of benzylamine, the red-brown solution deposits, after some hours, a crystalline mass, whence hydrochloric acid extracts cyanobenzylamine, which is precipitated by potash from the hydrochloric acid solution. It is homologous with cyanophenylamine, which it closely resembles, only being less soluble in alcohol or ether.

Melobenzylamine. Metoluidine. $C^{15}H^{17}N^3 = C^7H^9N.C^7H^8CyN$. (Wilson, *loc. cit.*)—When the vapour of chloride of cyanogen is passed over fused benzylamine, heat is evolved, and a resinous mass obtained, consisting of hydrochlorate of metoluidine; this is dissolved in water acidulated with hydrochloric acid, filtered, and mixed with potash; and the white precipitate thus produced, is boiled with potash, washed, and recrystallised from alcohol. Crystalline laminæ, sparingly soluble in cold, somewhat more in boiling water; crystallises best from a mixture of water and alcohol; readily soluble in hydrochloric acid: the solution gives with dichloride of platinum, a dark-yellow precipitate of *chloroplatinate*, which is insoluble in water or alcohol and may be dried at 100° C. It is homologous with melaniline (melophenylamine).

Secondary and Tertiary Amines containing Benzyl.

Benzylethylamine. Ethyltoluidine. $C^9H^{13}N = N.C^7H^7.C^2H^5.H$. (Morley and Abel, Chem. Soc. Qu. J. vii. 68.)—Benzylamine is heated with iodide of ethyl in a sealed tube for two or three days in a water-bath; the product freed from excess of iodide by heat; the resulting oil, which is hydriodate of benzylethylamine, distilled with strong potash, and the distillate rectified over solid potash. It is a colourless oil with a peculiar smell: specific gravity 0·9391 at 15°·5 C.; boils at 217° The *chloroplatinate* is a pale-yellow crystalline compound, soluble in water or alcohol, less so in ether: at 100° it becomes dark, and is decomposed. The *oxalate* and *sulphate* are crystalline.

Benzyldiethylamine. Diethyltoluidine. $C^{11}H^{17}N = N.C^7H^7.(C^2H^5)^2$.—Prepared in the same manner as the foregoing compound, benzylethylamine being substituted for benzylamine. A colourless, odorous oil: specific gravity 0·9242 at 15·5 C., boils at 229°. The *chloroplatinate* is a resinous non-crystalline mass. The *hydriodate* forms oily drops which crystallise when touched with a glass-rod; is very soluble in water, decomposes when exposed to the air, or in contact with alcohol.

Benzyltriethylium. $C^{13}H^{22}N = N.C^7H^7.(C^2H^5)^3$.—Known only in combination with acids. When benzyldiethylamine is heated with iodide of ethyl to 100° C. in a sealed tube till crystals are formed and excess of iodide of ethyl is removed by distillation, *iodide of benzyltriethylium* remains as a heavy oil. This is decomposed by heating with oxide of silver, yielding a solution of *hydrate of benzyltriethylium* $N.C^7H^7(C^2H^5)^3.H.O$, which is strongly alkaline, has a bitter taste, and precipitates most metallic salts. The *chloroplatinate* is insoluble in cold, soluble in hot water, whence it crystallises in fine needles; it loses platinum on recrystallisation.

Nitrobenzylamine. Nitrotoluidine. $C^7H^8N^2O^2 = N.C^7H^6NO^2.H^2$. (Cahours. Compt. rend. xxx. 320.)—Formed by the action of sulphide of ammonium on hydride of dinitrobenzene; it crystallises in yellow needles, forms definite compounds with nitric, hydrochloric, sulphuric, and phosphoric acids: yields alkalamides with the chlorides of benzene and cumyl.

Tribenzylamine. $C^{21}H^{21}N = N.(C^7H^7)^3$. (Cannizzaro, Cimento, iii. 397.)—When chloride of benzyl is heated with alcoholic ammonia to 100° C. in a sealed tube, ammonia passed into the cooled product, the resulting precipitate exhausted with ether, and the ethereal solution evaporated, this compound is obtained in shining laminæ, which melt at 91·3° C. to a colourless liquid, and at 360° volatilise with partial decomposition. It is sparingly soluble in cold water or alcohol, more so in boiling alcohol, still more in ether, forming alkaline solutions. The *hydrochlorate* crystallises in needles from hot water. The *chloroplatinate* forms orange-needles. F. T. C.

BENZYLENE. C^7H^6.—A hypothetical diatomic radicle, of which, according to Wicke (Ann. Ch. Pharm. cii. 356.) Cahours' chlorobenzol is the chloride. It has not been isolated; neither has its hydrate (benzylenic or benzolic alcohol,) $C^7H^6.H^2.O^2$, nor its oxide (benzylenic ether) C^7H^6O been obtained; the reason assigned by Wicke being that the former readily decomposes, yielding water and the latter compound, which in turn is readily converted into its isomer, hydride of benzoyl. Several compound ethers have, however, been obtained, representing the alcohol in which the 2 atoms of basic hydrogen are replaced by positive or negative organic radicles (see BENZYLENIC ETHERS). Hydrobenzamide $C^{21}H^{18}N^2$, should probably be regarded as a tertiary diamine containing this radicle. $N^2(C^7H^6)^3$. F. T. C.

BENZYLENE, CHLORIDE OF. *Chlorobenzol.* $C^7H^6Cl^2$. (Cahours (1848), Ann. Ch. Phys. [3] xxiii. 129. Wicke, Ann. Ch. Pharm. cii. 356.)—When hydride of benzoyl is brought into contact with a slight excess of pentachloride of phosphorus, a lively action takes place; and if, when this is over, a gentle heat be applied, oxychloride of phosphorus distils over at about 110° C., and chloride of benzylene at about 206°. The latter is washed with water, dried over chloride of calcium, and rectified. It is a colourless liquid, smelling faintly in the cold, but strongly when heated; insoluble in water, soluble in alcohol or ether: specific gravity 1·245 at 16°: vapour-density (expt.) 5·595; boils at 206°—208°. It is not oxidised by exposure to the air, or to oxygen. When heated in a water-bath with alcoholic *potash*, more slowly with aqueous potash to 100°, in a sealed tube, it yields chloride of potassium and hydride of benzoyl. *Ammonia*, whether dry, aqueous, or alcoholic, does not act upon it in the cold: when heated in a sealed tube to 100° with an ammonia-solution, it yields chloride of ammonium, and bitter-almond oil. It is not attacked by dry *cyanide of potassium* at 100°. Heated with alcoholic *sulphocyanate of potassium* to 100° in a sealed tube, it yields chloride of potassium, and an oil smelling like oil of mustard. Alcoholic *nitrate of silver* deprives it of all its chlorine, hydride of benzoyl being formed. Alcoholic *hydrosulphate of potassium* converts it into sulphide of benzylene.

Gerhardt (Traité, iii. 167) regards this compound as hydride of benzoyl in which oxygen is replaced by chlorine: Wicke, however, shows conclusively that it possesses none of the properties of an aldehyde. F. T. C.

BENZYLENE, SULPHIDE OF. *Sulphobenzol*, C^7H^6S. (Cahours, *loc. cit.*)—Formed by the action of alcoholic sulphydrate of potassium on chloride of benzylene, and recrystallised from boiling alcohol, in which it is readily soluble. White pearly scales, insoluble in water, which melt at 64° C. and crystallise on cooling: when further heated, it is partly volatilised, and partly decomposed. It is oxidised even by dilute nitric acid, with formation of sulphuric acid, and a substance soluble in alkalis, which crystallises in shining yellow scales. F. T. C.

BENZYLENE-PHENYLAMINE. *Benzosylanilide. Stilbylaniline.* $C^{13}H^{11}N = N.C^7H^6.C^6H^5$. (Laurent and Gerhardt, Compt. chim. 1850, 117.)—When perfectly dry hydride of benzoyl is mixed with about its own volume of perfectly dry phenylamine, water separates out, and a crystalline mass forms after a time (sometimes not until water is added): this is pressed between filter-paper, and recrystallised from hot alcohol, or purified by rectification. It forms beautiful shining laminæ, without taste or smell, insoluble in water, soluble in alcohol or ether. It is easily fusible, and boils at a very high temperature without decomposition. *Bromine* acts with violence on its alcoholic solution, forming after a time crystals of tribromophenylamine. With cold fuming *nitric acid*, it forms a dark-green solution, whence water precipitates hydride of benzoyl, nitrate of phenylamine remaining in solution: *sulphuric acid* decomposes it in a similar manner, forming a yellow solution. It becomes liquid by contact with *acetic* or *hydrochloric acid*: the latter dissolves it on boiling, without decomposition. It is scarcely attacked by boiling potash. F. T. C.

BENZYLENIC ETHERS. Salts or ethers of Benzylene. (Wicke, *loc. cit.*)

a. *Ethers containing a Positive Radicle.*

METHYLBENZYLENIC ETHER. *Methylate of Benzylene.* $C^9H^{12}O^2 = C^7H^6.(CH^3)^2O^2$.—A mixture of 1 at. chloride of benzylene with a solution of 2 at. sodium in absolute methylic alcohol, is heated for some hours, when chloride of sodium separates in abundance; the methylic alcohol is distilled off, and the residue mixed with water, when the ether rises to the surface, and is removed with a pipette, dried and rectified. It is a transparent, colourless liquid, heavier than water, with a pleasant smell like that of geraniums; insoluble in water, soluble in wood-spirit, alcohol, or ether. It boils at 208° C., leaving a brown residue arising from decomposition.

Ethylbenzylenic Ether. *Ethylate of Benzylene.* $C^{11}H^{16}O^2 = C^7H^6(C^2H^5)^2.O^2$.—Prepared precisely like the foregoing compound, ethylic being substituted for methylic alcohol. It boils at 222° C.: in other respects it resembles the methyl-compound.

Amylbenzylenic Ether. *Amylate of Benzylene.* $C^{17}H^{28}O^2 = C^7H^6.(C^5H^{11})^2.O^2$.—Prepared like the preceding compounds: but the ether must be separated by fractional distillation, not by addition of water. It is a slightly yellowish oil, smelling like fusel-oil, and lighter than water: it boils, not without considerable decomposition, about 292° C.

b. *Ethers containing Acid Radicles:*

The only one of these which has been obtained perfectly pure, and in the crystalline form, is

Acetobenzylenic Ether. *Acetate of Benzylene.* $C^{11}H^{12}O^4 = C^7H^6.(C^2H^3O)^2.O^2$—1 at. chloride of benzylene is triturated with rather more than 2 at. dry acetate of silver, and the mixture heated very gently in a flask; the reaction is so violent that it is well not to use more than 10 grm. silver-salt at a time. The product, when cool, is repeatedly extracted with ether; the extracts are distilled in the water-bath; and the yellowish oily residue is washed with weak soda-solution and with water, then redissolved in ether, and left to evaporate. A viscid oil is thus obtained, in which crystals gradually form, until at last it solidifies completely. It forms small white shining crystals, belonging to the monoclinic system, insoluble in water, soluble in alcohol or ether, whence it separates on evaporation as an oil, which often does not crystallise till agitated. It melts at 36° C., and crystallises on cooling: begins to boil at 190°, the temperature gradually rising to 240°, and yields a distillate consisting of acetic anhydride and hydride of benzoyl. Heated with aqueous potash or dilute sulphuric acid, to 100° in a sealed tube, it is converted into acetic acid and hydride of benzoyl: with aqueous ammonia under the same circumstances, it yields acetamide and hydrobenzamide.

Benzobenzylenic Ether. *Benzoate of Benzylene.* $C^{21}H^{16}O^4 = C^7H^6.(C^7H^5O)^2.O^2$.—Chloride of benzylene acts violently on benzoate of silver, with evolution of heat: the ethereal extract of the product yields on evaporation a viscid, brown, non-crystallisable mass. With alcoholic potash it forms immediately a solid mass of potassic benzoate, mixed with hydride of benzoyl.

Succinobenzylenic Ether. *Succinate of Benzylene.* $C^{11}H^{10}O^4 = C^7H^6.C^4H^4O^2,O^2$.—Prepared like the foregoing compounds: its ethereal solution is decomposed by evaporation or by washing with dilute soda, into succinic acid and hydride of benzoyl.

Sulphobenzylenic Ether. *Sulphate of Benzylene.* $C^7H^6SO^4 = C^7H^6SO^2.O^2$.—Prepared in the same manner. It is a red-brown, non-crystallisable oil.

Valerobenzylenic Ether. *Valerate of Benzylene.* $C^{17}H^{24}O^4 = C^7H^6.(C^5H^9O).\,^2O$.—Obtained like the acetate. On evaporating its ethereal solution, it remains as a thick, yellow, non-crystallisable oil, which is decomposed by distillation into valerianic acid and hydride of benzoyl.

Chloride of benzylene acts so violently on oxalate of silver, that no definite product can be obtained.

F. T. C.

BENZYLETHYLAMINE. BENZYLDIETHYLAMINE. BENZYLTRIETHYLIUM. (See Benzylamine.)

BENZYLIC ALCOHOL. *Hydrate of Benzyl. Benzoic Alcohol. Toluylic Alcohol.* $C^7H^8O = C^7H^7.H.O$. (Cannizzaro [1853], Ann. Ch. Pharm. lxxxviii. 129; xc. 252; xcii. 113; xcvi. 246; Scharling, *ibid.* xcvii. 168.)—Formed: 1. By the action of alcoholic potash on hydride of benzoyl:

$$2C^7H^6O + KHO = C^7H^8O + C^7H^5KO^2.$$

When a mixture of pure hydride of benzoyl with its own volume of absolute alcohol is mixed with 3—4 vols. alcoholic potash, of specific gravity 1·02, heat is evolved, and the whole solidifies to a crystalline magma. The potassic benzoate is dissolved out with hot water, the alcohol distilled off, the residue mixed with water till it begins to be turbid, and then shaken up with ether. The brown oily residue obtained by evaporating the ethereal solution, is dried over fused potash, and repeatedly rectified.—2. When acetate of benzyl, obtained by boiling chloride of benzyl with alcoholic acetate of potassium, is boiled with strong alcoholic potash, and the alcohol distilled off, the residual liquid separates into two layers, the upper of which contains benzylic alcohol, which is separated by fractional distillation.—3. Scharling has shown that the substance known as *peruvin*, obtained by the action of potash on cinnamein, is benzylic alcohol.

It is a colourless, strongly-refracting oil, with a faint pleasant smell: specific gravity 1·051 at 14°·4 C., 1·063 at 0° (Kopp): vapour-density (expt.) 3·85: boils at 206°·5, under pressure of 751·4 mm. (Kopp.) It is insoluble in water: soluble in all proportions in alcohol, ether, acetic acid, or bisulphide of carbon.

When its vapour is passed through a red-hot tube filled with spongy platinum, benzene with other compounds is formed. It is converted into hydride of benzoyl by *oxygen*, in presence of platinum-black, or by *nitric acid:* aqueous *chromic acid* converts it into benzoic acid. With strong *sulphuric acid*, *phosphoric anhydride*, or *chloride of zinc*, it yields a brown resin, insoluble in water, alcohol, or ether (probably stilbene). Fused *boric anhydride* converts it at 100°—120° C. into benzylic ether, at a higher temperature into stilbene (or benzylene?): with *fluoride of boron*, it yields the same product. Distilled with strong alcoholic potash, it yields hydride of benzyl (*q. v.*)

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BENZYLIC ETHER. $C^{14}H^{14}O = (C^7H^7)^2.O$. (Cannizzaro, Ann. Ch. Pharm. xcii. 115.)—Fused and pulverised boric anhydride is mixed into a paste with benzylic alcohol; the mixture is heated for some hours to 120°—125° C.; and the resulting hard brown mass is treated with water and a solution of alkaline carbonate, when a greenish-brown oil rises to the surface. When this is distilled, benzylic alcohol passes over below 300°, and benzylic ether at 300°—315°: the residue contains stilbene. Benzylic ether is a colourless, slightly fluorescent oil, boiling at 300°—315°. When heated above its boiling-point, it becomes yellow and is decomposed, yielding resinous stilbene, hydride of benzoyl, and a light oil, which is probably hydride of benzyl. With phosphoric anhydride or sulphuric acid, it yields the same product as benzylic alcohol.

Ethyl-benzylic Ether. $C^9H^{12}O = C^7H^7.C^2H^5.O$. (Cannizzaro, Cimento, iii. 397.)—Chloride of benzyl is distilled upwards with alcoholic potash, and the resulting liquid is decanted from the chloride of potassium, and mixed with water, when it separates into two layers: the upper of these is distilled, and the portion which comes over at 185° C. dried over chloride of calcium and rectified. Colourless, mobile liquid, with a pleasant smell; lighter than, and insoluble in, water: boils at 185°.

For the compound benzylic ethers containing acid radicles, see ACETIC and BENZOIC ACIDS.

F. T. C.

BERAUNITE. A hydrated sesquiphosphate of iron occurring at St. Benigna in the circle of Beraun in Bohemia, together with cacoxene and Dufrenite. It forms radiated or laminar masses, with perfect cleavage in one direction; imperfect at right angles to the first. Specific gravity 2·878. Hardness 2·0 to 2·5. Rather brittle.

BERBERINE. $C^{21}H^{19}NO^5$ (?)* An organic base discovered in 1837, by Buchner (Ann. Ch. Pharm. xxiv. 228), in the root of the barberry (*Berberis vulgaris*), and since found in other species of Berberis growing in Mexico and in India. It has also been obtained by Bödeker (Ann. Ch. Pharm. lxvi. 384; lxix. 40), from colombo-root (*Cocculus palmatus*); by Perrins (Ann. Ch. Pharm. lxxxiii. 276), from the colombo-root of Ceylon (*Menispermum fenestratum*); and by Stenhouse (Pharm. J. Trans. xiv. 455), in a yellow bark used as a dye by the natives of Abeoconta in West Africa.

Preparation. a. *From Barberry-root.*—The root is exhausted with boiling water; the extract concentrated by evaporation, and treated with warm alcohol of 82 per cent.; the solution filtered; the greater part of the alcohol distilled off; and the residue left to itself in a cool place. Yellow crystals of berberine are then deposited, and may be purified by recrystallisation from boiling water or alcohol. The root contains about 1·3 per cent. of berberine. (Buchner.)

b. From Colombo-root. — The dried alcoholic extract of the root is treated with hot water; the filtered solution neutralised with hydrochloric acid; and the liquid again filtered, treated with excess of hydrochloric acid, and left at rest for some days. It then deposits a crystalline sediment of hydrochlorate of berberine, which is dissolved in a small quantity of alcohol and reprecipitated by ether (Bödeker). For further purification, the hydrochlorate is converted into a sulphate; this salt is recrystallised and dried at 100° C.; the aqueous solution decomposed by baryta-water; the excess of baryta removed by passing a stream of carbonic acid through the liquid, then filtering, evaporating nearly to dryness, and digesting the residue in alcohol. The alcoholic solution is then precipitated by ether, and the precipitated berberine recrystallised from water. The same mode of purification may be adopted with berberine obtained from barberry-root. (Fleitmann, Ann. Ch. Pharm. xxiv. 228.)

Properties.—Small silky needles or concentrically grouped prisms of a light yellow colour. Odourless, but has a strong and persistently bitter taste. Sparingly soluble in water and alcohol when cold; easily at the boiling heat; insoluble in ether. Oils, both fatty and volatile, dissolve it in small quantity.

The crystals heated to 100° C. give off 19·26 per cent. (5 at.) water of crystallisation, and the residue contains 66·7 to 67·4 carbon, and 5·6 to 5·7 hydrogen, agreeing

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* Or rather $C^{20}H^{17}NO^4$ (Perrins, Chem. Soc. J. xv. 339). See APPENDIX.

nearly with the formula $C^{21}H^{19}NO^5.\frac{1}{2}H^2O$, or $C^{42}H^{19}NO^{10}.HO$ (Fleitmann). The remaining water cannot be expelled without further decomposition. According to Fleitmann, the anhydrous salts of berberine contain the group $C^{42}H^{18}NO^9$ associated with acids: *e.g.* the hydrochlorate = $C^{42}H^{18}NO^9.HCl$; berberine dried at 100° is $C^{42}H^{18}NO^9.2HO$, and the crystals contain $C^{42}H^{18}NO^9.2HO + 10\,aq$. These formulæ are, however, by no means probable, and further examination is required to determine the rational constitution of the base. The formula $C^{21}H^{19}NO^5$ or $C^{42}H^{19}NO^{10}$ is that suggested by Gerhardt (Traité, iv. 205).

Berberine melts at 120° C. to a resinous mass, without loss of weight. Between 160° and 200° C. it gives off yellow odorous vapours, which condense into a solid body insoluble in water, but very soluble in alcohol, and leaves an abundant residue of charcoal. Ammonia colours berberine yellow-brown, and dissolves it in nearly the same proportions as water. Berberine boiled with caustic potash-ley melts, and is converted into a resinous substance, sparingly soluble in water, easily in alcohol. According to Bödeker, berberine distilled with milk of lime or hydrate of lead, yields chinoline.

The *salts of berberine* are, for the most part, sparingly soluble in water; many of them may be prepared by treating the hydrochlorate with a salt of potassium. *Hydrochlorate of berberine*, $C^{21}H^{19}NO^5.HCl + 2H^2O$, crystallises in slender yellow needles, which give off their water of crystallisation (8·65 per cent.) at 100° C. With sulphide of ammonium containing excess of sulphur, it forms a fœtid brown-red precipitate containing sulphur. A hot alcoholic solution of the hydrochlorate mixed with a concentrated alcoholic solution of glycocine, yields on cooling, a mass of slender orange-coloured needles, sparingly soluble in water, which appear to contain $C^{21}H^{19}NO^5.HCl.C^2H^5NO^2$(?) The *chloroplatinate of berberine*, $C^{21}H^{19}NO^5.HCl.PtCl^2$ (?) is a yellow precipitate nearly insoluble in water. The *chlorate*, $C^{21}H^{19}NO^5.HClO^3$ (?) is a bulky yellow precipitate obtained by mixing the hydrochlorate with chlorate of potassium. It is moderately soluble in pure water, sparingly soluble in saline liquids. The acid *chromate*, $C^{21}H^{19}NO^5.Cr^2H^2O^4$ (?) is a bulky yellow precipitate, sparingly soluble in water, obtained by mixing the hydrochlorate with acid chromate of potassium. It is very soluble in hydrochloric and sulphuric acids. When strongly heated, it decomposes suddenly, yielding a large quantity of the yellow substance produced in the dry distillation of berberine. *Nitrate of berberine* forms yellow crystals sparingly soluble in cold water. The *acid sulphate*, $C^{21}H^{19}NO^5.SO^4H^2$(?) is deposited after a while in small yellow crystals on adding sulphuric acid to a dilute solution of the hydrochlorate.

BERENGELITE. *Berengela resin.*—A bituminous mineral found in the province of St. Juan de Berengela in Peru, about one hundred miles from Arica, where it occurs in amorphous masses of considerable extent, forming a sort of pitch-lake, like that of Trinidad (p. 426). It has a conchoïdal fracture, a dark brown colour, inclining to green, and waxy lustre; yields a yellow powder; has a resinous unpleasant odour and a rather bitter taste. Melts below 100° C., and after cooling remains soft and unctuous at ordinary temperatures. It dissolves readily in cold alcohol and in ether. It is used for caulking ships. According to Johnston's analysis (Phil. Mag. [3] xiv. 87), its formula is $C^{20}H^{30}O^4$.

BERESITE is a fine-grained granite containing pyrites, occurring at Beresowsk in the Ural, in the rocks in which the gold veins are found.

BERGAMOT, OIL OF. A volatile oil obtained by pressing the rind of a variety of orange, *Citrus bergamia*, cultivated in the south of Europe. The oil thus obtained is light-yellow or sometimes greenish or brownish-yellow; mobile, with a very agreeable odour and aromatic somewhat bitter taste. Specific gravity 0·869. It generally exhibits an acid reaction, arising from the presence of a small quantity of acetic acid. It solidifies a little below 0° C., and at ordinary temperatures deposits, after a while, a solid camphor or stearoptene.

Bergamot-oil is a mixture of two essential oils, the more volatile of which is isomeric with oil of turpentine and oil of lemon, $C^{10}H^{16}$; but it is difficult to separate this oil by simple distillation.

The less volatile portion which, when rectified, boils at 183° C. and has a density of 0·856, contains oxygen, and according to Ohme (Ann. Ch. Pharm. xxxi. 316), has the composition of a hydrate of oil of lemon, $3C^{10}H^{16}.2H^2O$. According to Soubeiran and Capitaine (J. Pharm. xxvi. 68, 509), this portion of the oil is not of constant composition, but yields by fractional distillation, oils continually increasing in amount of oxygen, from 3·37 to 16·14 per cent. (perhaps the oil was oxidised during the distillation). They find also that the first portions turn the plane of polarisation of a luminous ray to the right, but that the subsequent portions exhibit less and less of this power, and finally none.

Ohme's rectified bergamot-oil is not altered by caustic potash. Its vapour passed over red-hot lime yields a large quantity of benzene. It absorbs hydrochloric acid gas abundantly, forming a liquid compound, which, after being shaken up and distilled with water, has the specific gravity 0·896; boils at 183° C., and contains $C^{60}H^{100}Cl^2O$, or $6C^{10}H^{16}.2HCl.H^2O$.

Bergamot-oil placed in contact with phosphoric anhydride becomes heated, and afterwards yields by distillation an oil smelling like oil of turpentine, and having exactly the composition $C^{10}H^{16}$. The residue of the distillation contains a conjugated acid, *phosphobergamic acid*, which forms soluble salts with calcium and lead.

BERGAMOT-CAMPHOR, *Bergaptene*, *Stearoptene of bergamot-oil*, is a solid substance deposited by crude oil of bergamot after long keeping. It crystallises in needles, melts at 206° C., and volatilises without decomposition. It is odourless and dissolves in boiling water, alcohol, and ether. Strong sulphuric acid colours it red. Heated with nitric acid, it yields oxalic acid. It gives by analysis about 66·2 per cent. carbon and 3·8 hydrogen, numbers answering to the formula $C^3H^6O^2$, but the rational formula is not yet determined. (Mulder, Ann. Ch. Pharm. **xxxi.** 70; Ohme, *loc. cit.*)

BERTHIERIN. The name given by Beudant to a ferruginous mineral occurring in small grains, resembling iron-spar or brown iron ore; but whether it is a definite species or a mixture is not decidedly known. According to Berthier, it contains 12·4 per cent. silica, 74·7 protoxide of iron, 7·8 alumina, and 5·1 water. The same name is also applied to a mineral from Hayanges near Metz, of greyish-green or liver-brown colour, which, under the microscope, appears like an oolitic rock, consisting of a greenish amorphous mass, containing innumerable small flattened needles of brown iron ore.

BERTHIERITE or **HAIDINGERITE.** These names are applied somewhat indiscriminately to three minerals, containing protosulphide of iron, together with trisulphide of antimony.—*a.* $3Fe^2S.2Sb^2S^3$. Found at Chazelles in Auvergne, crystalline or massive, with imperfect cleavage in several directions. Specific gravity 4·284: hardness 2·0 to 3·0. Iron-black or dark steel-grey. Opaque with metallic lustre. Fuses readily before the blowpipe on charcoal, yielding antimonial fumes and deposit, and leaving a black magnetic slag (Berthier, Ann. Ch. Phys. [2] **xxxv.** 351).—*b.* $3Fe^2S.4Sb^2S^3$. Found in a mine near Chazelles. Fibrous, with granular transverse fracture, almost destitute of lustre (Berthier, Pogg. Ann. **xxix.** 458).—*c.* $Fe^2S.Sb^2S^3$ or $FeSbS^2$. Found at Anglar in the Département de la Creuse. Crystalline, composed of fine parallel fibres. Steel-grey, inclining to bronze (Berthier). Minerals having this composition are also found in other localities.

BERTHOLLETIA EXCELSA. A Brazilian tree belonging to the order *Lecythidaceæ.* The kernels of the fruit, called Brazilian or Pava nuts, contain sugar, gum, and a pale yellow odourless fat oil, which solidifies at 0° C., and contains stearin, palmitin, and elain. (Caldwell, Ann. Ch. Pharm. xcviii. 120.)

BERYL. $3Gl^2O . Al^4O^3 . 6SiO^2$ $Si^3G^3Al^2O^9$.—A mineral species comprising several varieties, among which are found two very beautiful and costly gems, viz. *emerald*, and *aquamarine* or *precious beryl.* The crystals belong to the hexagonal system, being regular six-sided prisms variously modified, sometimes by the truncation of the lateral edges, at other times of the terminal edges. The most ordinary combinations are ∞P . oP and ∞P . oP . P. (*fig.* 98); sometimes, however, much more complicated modifications occur, like *fig.* 99, composed of the hexagonal prism ∞P. the terminal face oP, the primary hexagonal pyramid P, a sharper hexagonal pyramid of the first order 2P, a pyramid of the second order 2 P 2, and a symmetrical 12-sided pyramid 3 $P\frac{3}{2}$, whose faces (denoted in the figure by *z*) replace the combination-edges between 2P2, and ∞P. The prismatic faces are often deeply striated in the vertical direc-

Fig. 98.

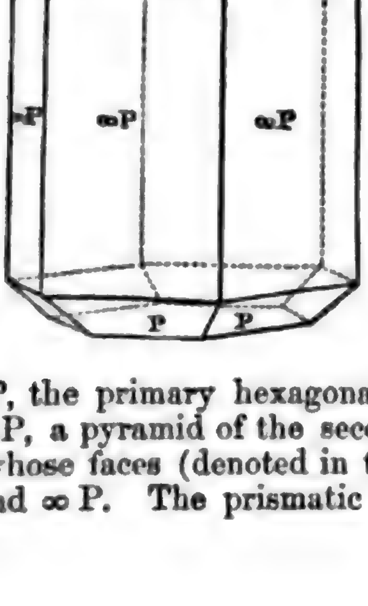
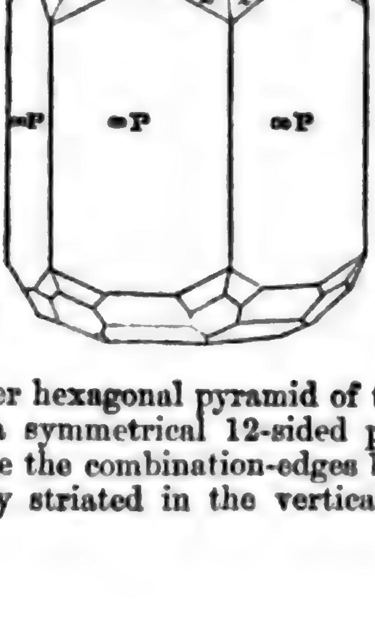


Fig. 99.



tion. Cleavage tolerably perfect, parallel to oP. Fracture conchoïdal and uneven. Specific gravity 2·67 to 2·76. Hardness 7·5 to 8·0. The most usual colour of the beryl is green, of various shades between yellow- and blue-green, arising from the presence of iron in various stages of oxidation; yellow, blue, rose-coloured, and colourless beryls are also found. The brilliant green of the emerald is due to the presence of oxide of chromium. Lustre vitreous. The best specimens of emerald and aquamarine are perfectly transparent; but the transparency is generally greatly diminished by cracks and striæ, the coarser varieties being opaque in the mass and translucent only at the edges. Beryl is difficult to fuse by itself before the blowpipe, melting to a glass at the edges only; with borax it fuses readily to a transparent glass; with phosphorus-salt, it leaves a skeleton of silica.

Beryl from Limoges was found by C. Gmelin to contain 67·54 SiO^2, 17·63 Al^4O^3, and 13·51 Gl^2O (= 98·68); a specimen from Fahlun, analysed by Berzelius, gave 68·35 SiO^2, 17·60 Al^4O^3, 13·13 Gl^2O, 0·72 Fe^4O^3 and 0·72 TaO^2. These and numerous other analyses agree nearly with the formula above given (calc. 67·46 SiO^2, 18·74 Al^4O^3, 13·80 GlO), which, by substituting $al = \frac{2}{3}Al$, may be reduced to that of a metasilicate $(Gl\mathit{al})\,SiO^3$.

Beryls are found in various parts of the world; the finest emeralds come from Peru, where they are found traversing clay-slate, hornblende slate, and granite; fine specimens are also obtained from Katharinenburg in Siberia; inferior varieties from the Heubach valley in the district of Pinzgau in Salzburg; varieties are also found in some old mines in Mount Zabarah in Upper Egypt, from which spot the ancients are supposed to have derived their emeralds. Fine transparent beryls or aquamarines are found in Brazil, in the granite district of Nertschinsk in Siberia, in the Ural and Altai mountains, and in the granite of the Morne mountains in the county of Down, Ireland. Opaque beryls, sometimes of very large size, are found at Langenbilau in Silesia; at Bodenmais in Bavaria, near Limoges in France; at Kinloch, Runnoch, and Cairngorm, Aberdeenshire; and in the counties of Dublin and Wicklow. Between the Connecticut and Marimac rivers, near Crofton in North America, enormous specimens have been found, measuring from 4 to 6 feet in length, and weighing between 2000 and 3000 pounds.

BERYLLIUM. Syn. with GLUCINUM.

BERZELIANITE. Selenide of Copper.

BERZELIITE. *Berzelite, Kühnite, Chaux arseniatè anhydre, Magnesian Pharmacolite.* $As^2(Mg^3Ca^3)O^8$.—A massive mineral occurring near Langbanshytta in Sweden. It has an uneven fracture, and exhibits traces of cleavability in one direction. Yellowish-white to honey-yellow, with waxy lustre; translucent on the edges. Perfectly soluble in nitric acid. Before the blowpipe, it exhibits the usual reactions of arsenic, and with soda shows evidence of a trace of manganese. (Kühn, Ann. Ch. Pharm. xxxiv. 271.)

BERZELIN. A mineral found in the older volcanic ejections near Lake Albano in Italy, together with hauyne, augite, and mica. It crystallises in octahedrons or dodecahedrons, belonging to the regular system, sometimes forming twin-crystals; cleavage tolerably distinct, parallel to the faces of a cube. The crystals are often uneven and rounded. It occurs also in spherical and stalactitic forms, massive and imbedded. Fracture varying from conchoïdal to uneven; colour white or grey; lustre vitreous to dull; varies from transparent to perfectly opaque; streak white; hardness 5·0; specific gravity 2·428 to 2·727. According to an imperfect analysis by L. Gmelin, its composition is similar to that of leucite. When pulverised and ignited, it yields a small quantity of water. Melts with difficulty before the blowpipe to a tumefied glass; with borax readily to a clear glass. Dissolves slowly in nitric acid, yielding a jelly of silica when heated. Similar crystals have been found in nephelin-dolerite from Meiches in Oberhessen. (Handw. d. Chem. ii. [1] 1023.)

The same name has been applied to native selenide of copper.

BERZELITE. This name has been given to Mendipite, Petalite, Thorite, and Berzeliite.

BETA. *Beet.*—A genus of plants, belonging to the natural order Chenopodiaceæ, distinguished by the large quantity of sugar contained in their roots. The three principal species are:—1. *Beta vulgaris*, common beet, well known for its sweet crimson roots, which are used as a salad.—2. *Beta cycla*, chard beet, inferior in the size and flavour of its roots, but distinguished by its remarkably thick-ribbed leaves, which are used in France in soups; or the ribs only are cut out and stewed like sea-kail.—3. *Beta altissima*, field-beet or mangold-wurzel, sometimes, though erroneously, regarded as a hybrid between the two former. This is by far the most important species, as it is extensively cultivated for feeding cattle, and in France and Germany also for the extraction of sugar.

The root of mangold-wurzel contains crystallisable sugar, identical in every respect with cane-sugar. Payen gives for the average composition of the root, 83·5 per cent. water, 10·5 sugar, 0·8 cellular substance and pectose, 1·5 nitrogenous matter (albumin, &c.), and 3·7 pectin and salts. The salts consist of nitrates and ammonium-salts, together with alkaline and earthy phosphates, sulphates, chlorides, oxalates and malates, or, according to some chemists, citrates. The root has also been stated to contain two or three peculiar acids, which have not been thoroughly examined. The dried leaves contain, according to Sprengel, 15·44 per cent. ash. The seed contains 11·6 per cent. water, and in 100 pts. of dry substance, 0·09 sulphur and 6·58 ash. (Way and Ogston.)

The following table exhibits the composition of the ash of the seed, leaves, and roots:—

	Ash of seed.	Ash of leaves.	Ash of roots.	
	Way.	Ogston.	Sprengel.	Ettl.
Potash (anhydrous) . . .	16·1	36·3	23·9	19·5—26·6
Soda " . . .	6·8	21·3	53·1	22·4—30·5
Lime	13·4	14·9	4·8	3·2— 4·5
Magnesia	15·2	5·4	2·2	7·0— 9·8
Alumina and ferric oxide . .	0·4	1·1	2·3	0·1— 0·1
Manganic oxide	1·8	0·4		
Silica	—	2·7	1·8	14·1—19·8
Sulphuric acid (anhydrous) . .	3·6	6·3	2·1	2·5— 2·5
Phosphoric " " . .	13·1	4·5	2·8	2·4— 2·4
Chlorine	—	6·9	6·3	1·4— 1·9
Carbonic acid (anhydrous) . .	13·8			
Chloride of sodium . . .	15·3			

BETULIN. $C^{48}H^{64}O^{3}$.—A resinous substance extracted from the outer bark of the birch-tree (*Betula alba*), or from the tar prepared therefrom. It was discovered by Löwitz (Crell. Chem. Ann. 1788, i. 302), and analysed by Hess (J. pr. Chem. xvi. 161). It belongs to the series of resins, including sylvic acid, which are produced by oxidation from hydrocarbons of the form $C^{5n}H^{8n}$. To extract it, the dried bark is exhausted with boiling water, then dried again and treated with boiling alcohol. The solution on cooling deposits the betulin, which is pressed, dried, and recrystallised from ether. It forms small crystalline nodules, which melt at about 200° C. The melted matter is colourless and transparent, and gives off vapours which smell like the bark when heated. It may be distilled in a current of air. It is not dissolved by alkalis.

BETULORETIC ACID. According to Kossmann (J. Pharm. [3] xxiv. 197) birch-resin consists of an acid, $C^{36}H^{66}O^{5}$, which is converted by nitric acid into picric acid, but is not decomposed by sulphuric acid.

BEUDANTIN. See NEPHELIN.

BEUDANTITE. A ferruginous mineral occurring at Horhausen and Montabaur in Nassau, and near Cork in Ireland. It crystallises in rhombohedrons cleavable parallel to the base, and having the rhombohedral faces horizontally striated. Colour black to olive-green. Streak light green. The fresh crystals have a waxy lustre. Hardness above 4·0. The Nassau mineral has a specific gravity of 4·0018, and melts readily before the blowpipe (Sandberger). The Irish variety has a specific gravity of 4·295, and is infusible (Rammelsberg). It contains sulphate of lead, associated with ferric sulphate, arsenate, and phosphate, the two latter replacing each other isomorphously; it also contains water (Pavy, Phil. Mag. [3] xxxvii. 161). According to Rammelsberg, it is $2(Pb^{2}O.SO^{3}) + Fe^{4}O^{3}.SO^{3} + 3Fe^{4}O^{3}.P^{2}O^{5} + 9H^{2}O$; according to Sandberger, $Pb^{2}O.SO^{3} + 3Pb^{2}O(As^{2}O^{5}; P^{2}O^{5}) + 3[3Fe^{4}O^{3}(As^{2}O^{5}; P^{2}O^{5})] + 24H^{2}O$. (Handw. d. Chem. ii. 1029.)

BEZETTA. *Tournesol en drapeaux. Schminkläppchen. Bezetta rubra et cærulea.*—A dye or pigment prepared by dipping linen rags in solutions of certain colouring matters. Red bezetta is coloured with cochineal, and is used as a cosmetic.

Blue bezetta (*Tournesol en drapeaux*), which is chiefly used for colouring the rind of Dutch cheeses, is prepared at Gallargues near Nîmes in the department of Gard, from a euphorbiaceous plant, *Chrozophora tinctoria* or *Croton tinctoria*. The fruits and the tops of the plants are gathered, and the juice being expressed, rags of coarse cloth are dipped into it, then dried, and afterwards exposed to the fumes of mules' or horses' dung. This last operation is called *aluminadou*. The cloths are turned from time to time, to ensure uniform coloration and prevent any part from being exposed too long to the fumes of the dung, which would turn them yellow. They are then dried a second time, again soaked in the juice, mixed this time with urine, and lastly exposed for some time to the action of the sun and wind. The quantity thus manufactured amounts to about 50 tons yearly. The blue of bezetta is reddened by acids, like litmus, though not so quickly, but differs from the latter in not being restored by alkalis. According to Joly, the same dye may be obtained from other euphorbiaceous plants, *Chrozophora oblongata*, *C. plicata*, *Croton tricuspidatum*, *Mercurialis perennis*, and *M. tormentosa*. The juice exists in all these plants in the colourless state, and turns blue only on exposure to the air. (Handw. d. Chem. ii. [1] 1030; Gerh. Traité, iii. 820.)

BEZOAR. This name, which is derived from a Persian word implying an antidote to poison, was given to a concretion found in the stomach or intestines of an animal of the goat kind, *Capra ægragus*, which was once very highly valued for this imaginary quality, and has thence been extended to all concretions found in animals.

According to Taylor (Phil. Mag. No. 186 p. 36 and No. 186 p. 192), bezoars may be divided into nine varieties:—1. Phosphate of calcium, which forms concretions in the intestines of many *mammalia*.—2. Phosphate of magnesium: semitransparent and yellowish, and of specific gravity 2·160.—3. Phosphate of ammonium and magnesium: a concretion of a grey or brown colour, composed of radiations from a centre.—4. Oxalate of calcium.—5. Vegetable fibres.—6. Animal hair.—7. Ambergris.—8. Lithofellic acid.—9. Ellagic or bezoardic acid.

Of true bezoars there are three kinds, *oriental*, *occidental*, and *German*. The true oriental bezoars found in the *Capra ægragus*, the gazelle (*Antilope Dorcas*), and other ruminant animals, are spherical or oval masses, varying from the size of a pea to that of the fist, and composed of concentric layers of resinous matter with a nucleus of some foreign substance, such as pieces of bark or other hard vegetable matter which the animal has swallowed. They have a shining resinous fracture, are destitute of taste and odour, nearly insoluble in water and aqueous hydrochloric acid, but soluble for the greater part in potash-ley. When heated, they emit an agreeable odour and burn away, leaving but a small quantity of ash. These characters suffice to distinguish the oriental bezoars from those varieties which contain a considerable quantity of inorganic matter. There are two kinds of them, the one consisting of ellagic, the other of lithofellic acid. The latter have a more waxy lustre and greener colour than the former, and are also distinguished by their smaller specific gravity, viz. 1·1, while that of the ellagic acid stones is 1·6. They contain, besides lithofellic acid, a substance resembling the colouring matter of bile, and are perhaps biliary calculi. Oriental bezoars are greatly prized in Persia and other countries of the East for their supposed medicinal properties. The Shah of Persia sent one in 1808 as a present to Napoleon.

The occidental bezoars are found in the lama (*Auchenia Lama*), and in *A. Vicunna*: they resemble the oriental in external appearance, but differ totally in their chemical characters, inasmuch as they consist chiefly of phosphate of calcium, with but little organic matter.

German bezoars, which are chiefly obtained from the chamois or gemsbock (*Antilope rupicapra*), consist chiefly of interlaced vegetable fibres or animal hairs bound together by a leathery coating.

BEZOARDIC ACID. Syn. of Ellagic Acid.

BEZOARDICUM ANIMALE. An antiquated medicament made from the dried hearts and livers of vipers, and supposed to be an antidote against poison: hence its name.

BEZOARDICUM MINERALE. A name applied by the older chemists to antimonic acid, especially to that prepared from butter of antimony by the action of nitric acid.

BI-COMPOUNDS. See Di-Compounds and Nomenclature.

BILDSTEIN. Syn. with Agalmatolite.

BILE. *Gall. Galle.* (Lehmann, "Physiological Chemistry," Cavendish Society's Edition, ii. 61; also Gmelin's Handbuch, viii. 38. Strecker, Ann. Ch. Pharm. lxv. 1; lxvii. 1; lxx. 149. Gundelach and Strecker, *ibid.* lxii. 205).—Bile, as secreted by the cells of the liver, is taken up by the biliary ducts, which unite to form the hepatic duct, by which the secretion is either discharged directly into the duodenum, or is conveyed through the cystic duct into the gall-bladder, wherein it becomes accumulated and to some extent inspissated. Cystic bile when taken from a healthy animal recently killed, is a mucous, transparent, ropy liquid, of green or brown colour. It has a bitter but not astringent taste, sometimes leaving a sweetish after-taste, and a peculiar odour, which, when the bile is warmed, is often very much like that of musk.

Its specific gravity is about 1·02. It does not diffuse itself readily through water, unless the mixture be stirred. Its reaction is, for the most part, faintly alkaline, sometimes neutral, never acid, excepting in peculiar states of disease. Bile in its ordinary state, before the mucus is removed, putrefies very readily; but when freed from mucus, it is much less prone to putrefactive decomposition.

The chemical composition of bile varies to a certain extent according to the nature of the animal which yields it; but every kind of bile contains two essential constituents, viz. a resinous and a colouring matter, associated with small quantities of cholesterin, fats, salts of fatty acids, and certain mineral salts, chiefly chloride of sodium and phosphates, with smaller quantities of phosphate and carbonate of sodium, phosphate of calcium, phosphate of magnesium, and extremely minute quantities of iron and manganese, but no alkaline sulphates. No salts of ammonia are found in fresh healthy bile, but during the putrefaction of bile, ammonia is produced. Bile also contains mucus mixed with cells of epithelium.

The *resinous matter of bile* is the most abundant and important of its constituents. It consists, in nearly all cases, of the sodium or potassium salts of two nitrogenised acids, one containing sulphur, the other free from that element. The former of these acids, called taurocholic acid, is resolved by the action of alkalis into *taurine* and *cholic acid*, a crystalline acid containing neither nitrogen nor sulphur, and changing, under certain circumstances, into an amorphous isomeric acid called choloidic acid, differing from it only by the elements of water:

$$\underset{\substack{\text{Taurocholic}\\\text{acid.}}}{C^{26}H^{45}NSO^7} + H^2O = \underset{\substack{\text{Cholic}\\\text{acid.}}}{C^{24}H^{40}O^5} + \underset{\text{Taurine.}}{C^2H^7NSO^3};$$

and the latter, called glycocholic acid, is resolved in like manner into cholic acid and *glycocine:*

$$\underset{\substack{\text{Glycocholic}\\\text{acid.}}}{C^{26}H^{43}NO^6} + H^2O = \underset{\substack{\text{Cholic}\\\text{acid.}}}{C^{24}H^{40}O^5} + \underset{\text{Glycocine.}}{C^2H^5NO^2}$$

All kinds of bile, excepting that of the pig, contain one or both of these acids. Pig's bile contains an acid called glyco-hyocholic acid, analogous to glycocholic acid, and, like that compound, resolvable by the action of alkalis into glycocine and hyocholic acid, an acid not containing nitrogen:

$$\underset{\substack{\text{Glycohyo-}\\\text{cholic acid.}}}{C^{27}H^{43}NO^5} + H^2O = \underset{\substack{\text{Hyocholic}\\\text{acid.}}}{C^{25}H^{40}O^4} + \underset{\text{Glycocine.}}{C^2H^5NO^2}.$$

The *colouring matter of bile*, *bile-pigment*, or *cholochrome*, is also a nitrogenised acid, and is decomposed by nitrous acid, with evolution of nitrogen and formation of a crystallised acid, *cholochromic acid*, which is free from nitrogen. (Thudichum, Chem. Soc. Qu. J. xiv. 114.)

The bile of carnivorous and omnivorous animals, including man, contains a brown pigment, the *cholepyrrhin* of Berzelius: that of birds, fishes, and amphibia has usually an intense green pigment, *biliverdin*. The brown pigment is always combined either with soda or with lime; in the latter case, it is insoluble, and appears in the form of brown granules when the bile is examined by the microscope.

The analysis of bile is conducted as follows:

The bile is first mixed with half its volume or more of 83 per cent. alcohol, which throws down mucus and epithelium; the precipitate is rinsed with spirit, then with water, afterwards dried and weighed.

The bile thus freed from mucus, is evaporated to dryness, first over the water-bath and then under the air-pump on a sand-bath heated to 100° C.; the residue is left to cool in vacuo, after which, air dried by passing over chloride of calcium is introduced into the receiver, and the weighing is completed as quickly as possible, because the dried bile is extremely hygroscopic.

The residue is next digested for a considerable time with *ether*, which takes up fat and cholesterin. The total quantity of these matters may then be determined by evaporating the ethereal extract; but the different substances contained in it cannot be separately estimated, unless very large quantities of bile are operated upon; in that case, the fatty acids (stearic and margaric or palmitic acids) may be separated from the cholesterin by precipitation as lead-salts.

The residue insoluble in ether, which contains the essential constituents of the bile, is next to be treated with cold *absolute alcohol*, which dissolves the salts of the biliary acids, together with part of the bile-pigment; the greater part of the alcohol is then removed by evaporation; ether added to the concentrated solution as long as any turbidity is produced; and the liquid left to stand for some time in a cool place.

The alkaline taurocholate and glycocholate are thereby precipitated, and their quantity may be estimated by washing the precipitate with ether, and weighing it after drying over the water-bath. It always, however, contains a certain portion of bile-pigment, which cannot be completely separated unless it consists of pure cholepyrrhin, in which case it may be separated by chloride of calcium. The quantity of soda or potash associated with the biliary acids and the bile-pigment, may be determined by decomposing a weighed portion of the ether-precipitate with sulphuric acid.

The taurocholic and glycocholic acids cannot be completely separated one from the other. An approximate separation may be effected by dissolving the precipitate in alcohol, and treating it with neutral acetate of lead, which precipitates only the glycocholic acid; but the best way of estimating the relative quantities of the two acids, is to determine the amount of ***sulphur*** in the ether-precipitate, by fusing it with nitre or by one of the other methods given under ANALYSIS (ORGANIC), p. 225. Every 6 pts. of sulphur correspond to 100 pts. of taurocholate of sodium.

The residue of the bile, insoluble in absolute alcohol, must now be determined with the view of checking the analysis. It contains pigment, partly free and partly combined with lime; also alkaline and earthy phosphates, with chloride and carbonate of sodium, very rarely sulphate of potassium, but often a little taurine; its amount is generally too small to allow of the quantitative separation of these substances, unless very large quantities of bile are operated upon. Altogether the determinations which have been made of the amount of pigment, cholesterin, fats, fatty acids, and mineral constituents of bile, cannot be regarded as more than approximations to the truth.

Pettenkofer's Test for Bile.—When bile is mixed with a strong syrup of sugar, and then with strong sulphuric acid, so that it becomes heated, it assumes a deep violet-red or purple tint, which disappears on addition of water. This reaction is produced by cholic, choloidic, glycocholic, and taurocholic acids (or the corresponding acids in pig's bile), but not by any other substance; it is, therefore, perfectly characteristic of bile, and affords a very delicate indication of its presence. The best mode of applying it for the detection of small quantities of bile in blood or other animal fluids, is as follows:—The alcoholic extract of the liquid to be tested for biliary matter, is dissolved in a little water, and mixed with a single drop of a solution of sugar (1 pt. of sugar to 4 pts. of water), and pure strong sulphuric acid is then added by small quantities, till the turbidity at first produced, disappears, cooling after each addition; it then for a few moments exhibits a yellowish colour, which, however, soon changes to a pale cherry-red, then to deep carmine, then to purple, and finally to an intense violet tint. For the success of the experiment, care must be taken not to add too much sugar; otherwise a black mass will be formed, which will completely mask the reaction. The temperature of the mixture must be allowed to rise to about 50° C. but not higher. The reaction takes place with any kind of sugar, and likewise with acetic acid.

Composition of the Bile of various animals.—***Human bile*** consists mainly of taurochlorate of sodium, with very little glycocholate (Gorup-Besanez). ***Ox-bile***, on the contrary, contains chiefly glycocholate (Strecker). ***Pig-bile***, as already observed, consists mainly of the sodium-salt of an acid analogous to glycocholic acid; viz. glycohyocholic acid (Gundelach and Strecker), together with a small quantity of a sulphuretted acid, yielding taurine by decomposition: ***tauro-hyocoholic acid***; it likewise contains a very strong base containing sulphur.

The bile of most other animals consists mainly of taurocholate of sodium or potassium. That of the ***dog*** contains only taurocholate of sodium; that of the ***sheep***, and that of the *kangaroo* contain taurocholate, with very little glycocholate. In the bile of several kinds of fish, viz. *turbot*, *cod*, *pike*, and ***perch***, Strecker found taurocholate, with mere traces of glycocholate; a similar result was obtained by Schlossberger (Ann. Ch. Pharm. cviii. 166) with the bile of the ***shad-fish***. According to (Bensch (Ann. Ch. Pharm. lxv.) and Strecker, the bile of ***sea-fish*** contains potassium-salts, that of *fresh-water fish* chiefly sodium-salts. The bile of the ***Boa Anaconda*** (Schlieper, Ann. Ch. Pharm. lx. 109) and that of the ***Python tigris*** (Binder, *ibid.* cii. 91) consist mainly of taurocholate. *Goose-bile* appears likewise to consist essentially of taurocholate of sodium, though Marrson (Arch. Pharm. [2] lviii. 138), and more recently Heintz and Wisliscenus (Pogg. Ann. cviii. 547) state that the sulphuretted acid of goose-bile differs in composition from taurocholic acid; Heintz and Wisliscenus assign to it the composition $C^{29}H^{49}NSO^{6}$; but the analyses are not quite satisfactory.

Taurocholate of sodium contains about 6 per cent. of sulphur: now in the dried bile of the dog, Bensch found 6·2 per cent, sulphur; in that of the fox, 5·96 per cent.; of the wolf 5·03; of the bear 5·75; of the pig 0·32; of the calf 5·62; of the sheep 6·46; of the goat 5·99; of the domestic fowl 5·57; and of several fishes 6·46 per cent.

In normal human bile, Frerichs found 14 per cent. or rather more of solid ***constituents;*** Gorup-Besanez, in the bile of two recently executed criminals, found 10·19 and 17·73 per cent. solid matter; in that of an old man, 9·13 per cent; and in that of a boy of twelve years old, 17·19 per cent. solid matter. Ox-bile contains 10·13 per cent. solid constituents; pig's bile 10·6 to 11·08 per cent. (Gundelach and Strecker); dog's bile 5·1 per cent.; cat's bile 5·6 per cent. (Bidder and Schmidt); sheep's bile 5·3; rabbit's bile 1·8; goose bile 6·9; kangaroo's bile 14·13; and crow's bile 7·3; per cent. solid constituents. The concentration of the bile appears to increase with the time it remains in the gall-bladder.

The proportion of *ash* in the dried residue amounts in normal human bile to 6·14 per cent. Gorup-Besanez), in ox-bile to 12·7 (Berzelius); in calf's bile to 13·15 (Bensch); in sheep's bile to 11·86; in goat's bile to 13·21; in pig's bile to 13·6; in fox bile to 12·71; in that of the domestic fowl to 10·99; in that of fresh-water fish, to 14·11 per cent.; in that of the fresh-water turtle (*Emys geographica*) to 5·5; and in that of the salt-water turtle (*Emys insculpta*) to 6·3 per cent. (Wetherill, J. pr. Chem. lxxvi. 61). The fresh bile of *Python tigris* yields 1·21 per cent. of ash.

Ox-bile extracted from the gall-bladder without pressure, contains 0·134 per cent. *mucus;* human-bile 0·158 per cent. (Lehmann); Gorup-Besanez found in human bile 1·45 and 2·21 per cent. *mucus* and *bile-pigment.* The bile of the kangaroo contains 4·34 per cent. *mucus* and *colouring matter*, and 1·09 *cholesterin* and *fat;* that of the shad-fish contains 1·28 per cent. *mucus* and *colouring-matter*, and 0·23 per cent. *fat;* that of *Python tigris*, contains 0·89 per cent. *mucus* and 0·03 *fat;* goose-bile contains 2·56 per cent. mucus, 0·36 *fat* and *cholesterin.* (Marrson.)

The bile, like all the other normal secretions, is liable to alteration from disease, and sometimes contains heterogeneous constituents. *Albumin* is sometimes found in it, especially in fatty liver, in Bright's disease, and in the embryonic state. *Urea* has been found in the bile, in cases of fatty degeneration of the kidneys, and in animals whose kidneys have been extirpated; also in cholera. Bizio once discovered a dark-red non-bitter bile in a patient suffering from jaundice; it contained an emerald-green pigment, to which he gave the name of *erythrogen*, from its volatilising at 40° C. and giving off a red vapour. A similar substance was found by Lehmann in a case of acute yellow atrophy of the liver. In the bile of a child who died suddenly, Lehmann found a considerable quantity of *sulphide of ammonium*, but the previous history of the case was not known.

The normal constituents of the bile also vary in proportion, in various cases of disease. The bile has been found to be poor in solid constituents, in persons who have died from severe inflammatory affections, especially from pneumonia, and likewise in fatal cases of dropsy; it also contains an excess of water in diabetes, and in certain cases of typhus; in other cases of that disease, however, the bile becomes thicker than in health. The solid constituents of the bile are commonly *increased* in those abdominal diseases in which the motion of the blood in the larger veins is impeded, and in certain cases of heart-disease, in which the blood accumulates in excessive quantity in the hepatic veins. In cholera, the bile is also found to be dense, tough, and consistent. The proportion of *mucus* is often increased when the bile is very dilute; indeed in typhus, the gall-bladder sometimes contains scarcely anything else, the resinous constituents being almost, if not altogether absent; the same is observed in catarrh of the biliary ducts. (Lehmann.)

The separation of *crystals of cholesterin*, which is sometimes, though rarely, observed in morbid bile, appears to be associated with an increase in the relative quantity of that substance; this phenomenon has been observed by Gorup-Besanez in very concentrated bile. *Free fat* is always present in the bile, but in the normal state is held in solution by the taurocholate of sodium; fat globules have, however, been observed by Gorup-Besanez in the bile of persons who have died from typhus, and from tuberculosis in the colliquative stage. (Lehmann.)

The bile is very seldom *acid;* an acid reaction has been observed in typhus, but it may have arisen partly from spontaneous decomposition after death, partly from effusion of pus into the gall-bladder: for pus, when contained in an enclosed space, often becomes acid with great rapidity. (Lehmann.)

Putrefaction of Bile.—When bile is left to itself, either in a closed or in an open vessel, it undergoes gradual decomposition, acquiring an offensive odour and acid reaction, and yielding a solid deposit containing cholic acid and other substances. Thudichum (Chem. Soc. Qu. J. xiv. 118) found that ox-bile left for a year or two in large bottles, well stoppered, and completely filled with it, had assumed a slight acid reaction, a bright port wine colour, and had deposited a copious, flaky, green and brown deposit, mixed with white chalk-like particles and greenish crystals. This deposit was found to consist of cholochrome (bile-pigment) cholic acid, phosphate of calcium and magnesium in dichroic crystals, and mucus. The fluid part of the bile was found to contain principally choloidate of sodium with a little cholate; also taurine, valerate and acetate of sodium, and of ammonium, and phosphate of sodium, but no glycocine, glycocholic acid, or taurocholic acid. The decomposition appears to begin by the resolution of the glycocholate of sodium into cholate of sodium and glycocine, and of the taurocholate into cholate and taurine. The ammonia and acetic acid are probably formed by the decomposition of the glycocine (oxyacetamic acid); the origin of the valeric acid is obscure; these acids unite with a portion of the soda and precipitate some of the cholochrome and cholic acid, the rest of that acid remaining in solution as choloidate of sodium. From the experiments of Gorup-Besanez (Ann. Ch. Pharm. lix. 129) it appears that bile allowed to decompose in an open vessel, at a comparatively high temperature, 25° to 30° R., deposited chiefly choloidic acid, but when the decomposition took place in a cellar at 10° to 12° R., cholic acid was deposited instead of choloidic, the higher temperature favouring the transformation of cholic acid into its amorphous modification.

Human bile putrefies much in the same manner as ox-bile; but the actual products are usually modified by the decomposition of the albumin which is present in nearly all the bile that can be obtained for examination, viz. the bile of persons who have died of disease, and usually not obtained till some days after death. The alkaline products resulting from the decomposition of the albumin partially neutralise the acid products of the decomposition of the bile, and thereby prevent, to a certain extent, the formation of insoluble compounds. (Thudichum.)

Biliary calculi, or *Gall-stones.*—These concretions in man sometimes consist chiefly of chlolochrome, held together by some binding material, generally supposed to be mucus, or inspissated bile, but consisting, according to Thudichum (*loc. cit.*), of cholic or choloidic acid, or both. In most cases, a small nucleus of this character is formed, and becomes coated with cholesterin, which then forms the chief mass of the concretion. Earthy phosphates and carbonates are likewise present. Ox gall-stones consist mainly of cholochrome, cholic acid, and choloidic acid, with small portions of cholesterin, and unaltered bile mechanically enclosed: they also contain the phosphates and carbonates of calcium and magnesium, and an ammonia-compound, possibly sulphide of ammonium (Thudichum). The formation of these calculi is attributed by Thudichum to a decomposition of the bile, similar to the putrefaction which takes place when it is removed from the gall-bladder. (See Gall-Stones.)

BIMSTEIN. See Pumice-Stone.

BINARY THEORY OF SALTS. The theory which regards salts as compounds of a metal with an acid or chlorous radicle: *e. g.* acetate of potassium = $C^2H^3O^2.K$: nitrate of potassium, $NO^3.K$, &c. (See Acids.)

BINNITE. A native sulpharsenite of lead, from the Binnenthal in the Valais, where it is found imbedded in white granular dolomite. It sometimes forms distinct prismatic crystals, belonging to the rhombic system, but more frequently, broad, reedlike, crystalline aggregations, or crude masses: it is very brittle and friable. Colour, steel-grey to iron-black, or light lead-grey, with strong metallic lustre. Opaque. Streak reddish-brown. Hardness, 2·5 to 3·0. Specific gravity 5·0 to 5·5. Its composition appears to be liable to some variation. According to Waltershausen, it is a mixture in variable proportions of ***arsenomelane***, $Pb^2S.As^2S^3$, and ***scleroclase***, $2Pb^2S.As^2S^3$. (Handw. d. Chem. ii. [1] 1099.)

BIOTIN. Syn. with Anorthite.

BIOTITE. Uniaxial or Magnesia Mica. See Mica.

BIRCH. (*Betula alba.*)—The *bark* of this tree contains, according to John (Repert. Pharm. xxxiii. 327), one-third of its weight of resin, and a considerable quantity of tannin, whence it is used for tanning leather, and for black-dyeing, especially of silk. The white, easily separated epidermis of birch-bark, contains resin, tannic acid, extractive matter, and ash, consisting chiefly of sesquioxide of iron, silica, and lime. The red-brown bark on the lower parts of the stem of an old tree, yields by successive treatment with ether, alcohol, and aqueous potash, a resin, $C^{20}H^{30}O^2$, soluble in ether, a red-brown colouring matter, $C^{16}H^8O^2$, soluble in alcohol, and another red-brown substance, $C^{20}H^{18}O^9$, soluble in alkalis, and precipitated by acids. (Stahelin and Hochstetter, Ann. Ch. Pharm. li. 79.)

The *leaves* of the birch contain, according to Grossmann, 0·3 per cent. essential oil and wax, besides tannin, and a bitter yellow colouring matter. They are used as fodder in northern countries.

The dry *wood* of the birch contains, according to Karsten, 0·25 to 0·3 per cent. ash; according to Berthier 1·0 per cent. Berthier found also in 100 pts. of the ash, 16 pts. of soluble and 84 pts. of insoluble salts. Wittstein (Pharm. Centralb. 1851, p. 404), has analysed the ash of birch-wood growing on different soils: viz. *a.* on the palagonitic soil of Akareyri in Iceland, composed of weathered volcanic rocks; *b.* on the sterile calcareous soil of Morschen in Kurhessen, belonging to the Muschelkalk formation; *c.* on the sandy soil of Marburg in Kurhessen, belonging to the sandstone formation.

	a	*b*	*c*		*a*	*b*	*c*
K^2O	12·8	5·7	14·8	SO^3	0·02		
Na^2O	1·6	1·2	2·8	SiO^2	2·9	1·5	4·0
Ca^2O	26·7	46·9		CO^2	18·8	24·6	12·9
Mg^2O	2·2	1·7	11·8	P^2O^5	8·1	4·2	16·6
Al^4O^3	1·4	0·4		H^2O	4·1	7·1	9·8
Fe^4O^3	0·8	0·4		Charcoal	0·6	0·4	0·5
Mn^4O^3	trace	1·7	3·8	Sand	19·8	2·4	4·7

Birch-fungus.—The fungus of the birch-tree contains woody fibre, phoblaphene (a substance also contained in pine-bark), fat, a bitter principle, uncrystallisable sugar, tannin, malic acid, tartaric acid, and citric acid. It yields 15·3 per cent. water, and 1·2 per cent. ash, containing in 100 pts.: 5·0 K^2O; 4·1 Na^2O; 48·8 Ca^2O; 5·5 Mg^2O; 3·1 Al^4O^3; 1·6 Fe^4O^3; 4·4 SO^3; 0·6 Cl; 15·6 P^2O^5; 4·7 SiO^2; 15·9 CO^2. (J. Wolff, Vierteljahrschrift f. prakt. Pharm. iii. 1.)

Birch-juice. Birch-water.—This liquid is obtained, like the juice of the maple, by boring the stems of the trees in February and March. A tree of average size yields about 8 litres of juice, consisting chiefly of sugar, together with nitrogenous substances and various salts, including acid tartrate of potassium. It easily ferments, and quickly turns sour when exposed to the air. In some localities, as in the Harz, in Courland, and in Livonia, it is used for the preparation of an effervescent wine.

Birch-oil.—All parts of the birch-tree appear to contain an essential oil. The young leaves and buds yield, by distillation with water, a colourless oil, which gradually turns yellow in the air, has the aromatic odour of newly developed birch-leaves, and a taste mild and sweetish at first, afterwards balsamic and burning. It is mobile at 14° C., becomes viscid at 0°, and solidifies to an amorphous mass at −10°. It dissolves in alcohol more readily than in ether: water is said to extract a stearoptene (?) from it. (Grossmann, Répert. Pharm. xxiii. 327.)

The bark of the *Betula lenta*, a North American tree, yields an essential oil identical with oil of wintergreen (salicylate of methyl): it does not however exist in the bark ready formed, but is produced from a crystalline substance, *gaultherin*, contained in the bark, by the action of a ferment in presence of water, in the same way as bitter-almond oil from amygdalin. (Procter, Amer. J. Pharm. Jan. 1844.)

Birch-Resin. See Betulin.

Birch-Tar. *Dagged. Black Doggert* or *Deggelt. Birch-tar Oil.*—In Russia and other northern countries, the bark of the white birch is subjected to a kind of downward distillation, in conical pits 20 or 25 feet deep, covered over first with a roofing of straw, and then of turf and mould, having holes to regulate the admission of air, as in the charcoal meilers. By this process, two products are obtained, namely, charcoal and tar, the latter amounting to 60 or 70 per cent. of the bark. It is a brown-black viscid liquid, used for coating wood, and also for lubricating carriage wheels, as it remains liquid even at very low temperatures.

This tar when distilled yields a brown strong-smelling acid oil, and on rectifying this oil, a liquid hydrocarbon, having the composition of oil of turpentine, passes over at 100° C., mixed with an oxygenated oil, the proportion of the latter gradually increasing as the distillation advances. The oxygenated oil may be removed by potash-ley, and the hydrocarbon, $C^{10}H^{16}$, is left behind. Its smell is like that of oil of turpentine, but more agreeable, recalling that of birch-bark. Specific gravity 0·87 at 20° C. Boils at 156°. Vapour-density 5·2 (calculation 2 vols. 4·8). At −16° it deposits a small quantity of stearoptene. Sparingly soluble in water, readily in alcohol and ether. It absorbs oxygen rapidly from the air, giving off carbonic anhydride, and being converted into a resinous mass. It is also oxidised by nitric acid, giving off hydrocyanic acid, and yielding two acid resins. It absorbs 32 per cent. chlorine, without forming a crystalline compound. Betulin is perhaps formed from this hydrocarbon by oxidation. (Sobrero, J. Pharm. [3] ii. 207.)

BIRDLIME. The best birdlime is made of the middle bark of the holly, boiled seven or eight hours in water, till it is soft and tender; then laid in heaps in pits in the ground and covered with stones, the water being previously drained from it; and in this state left for two or three weeks to ferment, till it is reduced to a kind of mucilage. This being taken from the pit, is pounded in a mortar to a paste, washed in river water, and kneaded, till it is free from extraneous matters. In this state it is left four or five days in earthen vessels, to ferment and purify itself, when it is fit for use.

It may likewise be obtained from the mistletoe, the *Viburnum lantana*, young shoots of elder, and other vegetable substances.

It is sometimes adulterated with turpentine, oil, vinegar, and other matters.

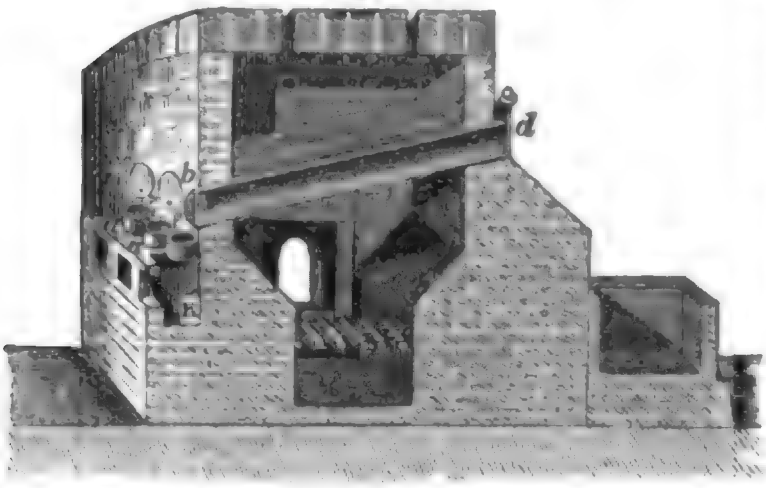
Good birdlime is of a greenish colour, and sour flavour; gluey, stringy, and tenacious, and in smell resembling linseed oil. By exposure to the air, it becomes dry and brittle, so that it may be powdered; but its viscidity is restored by wetting. It reddens tincture of litmus. Exposed to a gentle heat, it liquefies slightly, swells in bubbles, becomes grumous, emits a smell resembling that of animal oils, grows brown, but recovers its properties on cooling, if not heated too much. With a greater heat, it burns, giving out a brisk flame and much smoke. The residue contains sulphate and chloride of potassium, carbonate of calcium, and alumina, with a small portion of iron. U.

BISMUTH. *Symbol* Bi. *Atomic weight* 208 (Schneider); 210 (Dumas).— The metal bismuth has long been known, but was formerly often confounded with tin and lead. It is principally found in the metallic state, but also occurs in combination with sulphur, oxygen, and tellurium. In Cornwall and Cumberland it is found associated with ores of cobalt, and in Siberia with lead, in the form of *needle-ore* or *bismuth-lead-ore*.

For the arts it is prepared almost exclusively from native bismuth, and the great source for it is Saxony, where it occurs in metallic veins in gneiss and clay-slate, accompanying ores of silver, copper, lead, and tin.

The process of extraction is very simple, the mineral being merely heated in close vessels, so as to melt the bismuth, and thereby separate it from the gangue, or accompanying rock. The fusion is performed in iron tubes, laid in an inclined position, in a furnace (*fig.* 100). The ore is introduced at the upper end, *d*, which is then plugged. The other end, *b*, is closed with an iron plate having an aperture, *o*, through which the melted metal runs into earthen pots, *a*, heated by a few coals placed in the space, K, below, so as to keep the metal in the melted state. It is then ladled out and run into moulds. (See *Ure's Dictionary of Arts, Manufactures, and Mines*, i. 304.)

Fig. 100.



As thus prepared, the metal is impure, containing sulphur and arsenic, copper, nickel, iron, and other metals. It may be purified by placing it in a crucible with about $\frac{1}{10}$ its weight of nitre, and keeping it melted at a temperature not too much above its point of fusion, the mixture being continually stirred. The nitre, at first liquid, soon solidifies, forming with the impurities a slag, which collects on the surface of the metal. By repeating this operation a second time, the metal is obtained pure.

Small quantities of bismuth existing in lead-, copper-, and silver-ores, often become concentrated in the secondary products of metallurgic operations, especially in the process of separating silver from lead by cupellation. The lead oxidises faster than the bismuth, so that towards the end of the operation a blackish litharge is obtained, containing bismuth; and by reducing this mixed oxide, and again expelling the resulting alloy of lead and bismuth, the lead is oxidised and metallic bismuth remains. (Jahresber. d. Chem. 1859, 711.)

To obtain chemically pure bismuth, the metal is dissolved in nitric acid; and to the clear solution, a large excess of water is added, which precipitates the bismuth as basic nitrate, the other substances remaining in solution. The precipitate is well washed, dried, mixed with black flux, and reduced at a gentle heat in a crucible, at the bottom of which a regulus of pure metal is found.

Properties. — Bismuth is a metal of a greyish-white colour, with a distinct roseate tinge. When pure, it crystallises more readily than any other metal. It may be obtained in beautiful crystals by the following method. A few pounds are melted in a crucible, and then poured into an earthen dish previously made hot. When the surface of the metal has become covered with a crust, it is pierced on two opposite points with a rod of red hot-iron, and the liquid metal allowed to run out. On afterwards carefully removing the crust, the sides of the interior are found lined with beautiful crystals, often in pyramidal cubes like the crystals of chloride of sodium. They possess an iridescent lustre, arising from a very thin film of oxide which has been formed on their surface while still hot, and exhibits the colours of thin plates. Native bismuth crystallises in cubes, and combinations of the cube with the octahedron; also in regular tetrahedrons, with cleavage very distinct, parallel to the faces of the octahedron (Kopp's

Krystallographie). In Dana's *Mineralogy* (iii. 20), on the other hand, the crystalline form is stated to belong to the hexagonal system. Bismuth appears therefore to be dimorphous. Its specific gravity is 9·83, and it exhibits the singular anomaly, that when it has been exposed to great pressure, its density becomes less. Pure bismuth which has been exposed to a pressure of 200,000 pounds, was found to have the specific gravity 9·556. It melts at 264° C., and expands about $\frac{1}{32}$ in solidifying. Hence its specific gravity is greater in the liquid than in the solid state. At a high temperature, it may be distilled, and then sublimes in laminæ. It is very brittle, has a laminated, crystalline fracture, and is easily reduced to powder. Of all metals it exhibits in the highest degree the phenomena of diamagnetism.

Exposed to dry or moist air, it does not alter, but when exposed in contact with water in an open vessel, it becomes covered with a film of oxide of bismuth. Heated in the air, it burns with a bluish flame, forming yellow fumes. It decomposes water at high temperatures only. Concentrated hydrochloric acid acts on it with difficulty; sulphuric acid attacks it only when hot and concentrated. Nitric acid briskly attacks it and effects complete solution.

Bismuth forms three classes of compounds in which it is *di-*, *tri-*, and *pent-atomic*, respectively. The tri-atomic compounds are the most stable and the most numerous, *e. g.* $BiCl^3$, BiI^3, Bi^2O^3. Several di-atomic bismuth-compounds are also known, viz. $BiBr^2$, $BiCl^2$, BiI^2, Bi^2O^2, and Bi^2S^2. The only pent-atomic bismuth-compounds hitherto obtained are the pent-oxide Bi^2O^5, together with the corresponding acid and salts. E. A.

BISMUTH ACICULAR. Plumbo-cupreous sulphide of bismuth. See NEEDLE-ORE.

BISMUTH, ALLOYS OF. Bismuth unites readily with other metals, forming easily fusible compounds.

A native *arsenide of bismuth* containing 3 per cent. of the latter metal, occurs at Palmbaum, near Marienberg. It has a radiated texture like native sulphide of antimony. Specific gravity 5·392. Hardness = 2 (Breithaupt). 14 pts. of bismuth fused with 1 pt. of arsenic yield an alloy which expands strongly in solidifying.

Antimony unites in all proportions with bismnth, forming brittle alloys; that which contains equal parts of the two metals expands considerably in solidifying.

The most remarkable alloy of bismuth is that known as "fusible metal," which consists of 1 pt. of *lead*, 1 of *tin*, and 2 of *bismuth*. It melts at 93·75 C. According to Erman, it dilates in an anomalous manner when heated. It expands regularly from 32° to 95° C., and then contracts gradually to 131°; at which point it occupies a less bulk than it did at 32°; it then expands till it reaches 174°, and from that point its expansion is uniform. On account of this property of expanding as it cools, while still in the soft state, it is much used for taking impression from dies, as even the faintest lines are reproduced with minute accuracy. An alloy of bismuth with potassium is obtained when bismuth is fused with cream of tartar, 5 pts. bismuth to 4 pts. tartar. (For the other alloys of bismuth see the several metals.) E. A.

BISMUTH, BROMIDES OF. The *tri-bromide*, $Bi'''Br^3$, is formed by heating bismuth with excess of bromine. It is a steel-grey substance, like fused iodine; melts at 200° C., and boils at a dull red heat, with formation of hyacinth-red vapours. Heated with metallic bismuth, it yields a brown crystalline mass, probably a *di-bromide* $BiBr^2$, but it has not been obtained pure. (Weber.) E. A.

BISMUTH, CHLORIDES OF. *Trichloride*, $B'''Cl^3$.—Bismuth and chlorine readily combine, with evolution of heat and light if the metal be finely divided. On heating bismuth in a tubulated retort, in a current of chlorine, trichloride of bismuth distils as a white easily fusible substance. It readily attracts moisture from the air, becoming converted into a crystallised hydrate. The same substance is produced when bismuth is dissolved in aqua-regia, and the excess of acid evaporated. Chloride of bismuth dissolves in water containing hydrochloric acid; by pure water it is decomposed into hydrochloric acid, which dissolves a portion of the chloride, and a precipitate consisting of oxychloride of bismuth:

$$BiCl^3 + H^2O = BiClO + 2HCl.$$

When a solution of nitrate of bismuth is poured into solution of common salt, a white crystalline precipitate is formed, which is also *oxychloride* of bismuth, $BiCl^3.Bi^2O^3$ or $BiClO$. It is used for paint, and is known as "pearl white." Chloride of bismuth forms crystallisable double salts with the chlorides of potassium, of sodium, and of ammonium. They are isomorphous with, and analogous in composition to, the corresponding double chlorides of antimony.

DICHLORIDE OF BISMUTH, $BiCl^2$, is produced by heating the trichloride with metallic bismuth, also by the direct action of chlorine upon bismuth, provided the action be moderated by confining the current of chlorine to the upper part of the retort. Partial reduction of the trichloride is likewise effected by phosphorus, zinc, tin, mercury, and silver. The dichloride is a brown crystalline mass easily fusible and easily decomposed by water or by a strong solution of sal-ammoniac. At a high temperature, it is resolved into metallic bismuth and trichloride. (R. Weber, Pogg. Ann. cvii. 596.) E. A.

BISMUTH CUPREOUS. See TANNENITE and WITTICHITE.

BISMUTH, DETECTION AND ESTIMATION OF. *Blowpipe reactions.*—All bismuth-salts, and likewise the sulphide, are easily reduced by mixing them with carbonate of sodium, and heating the mixture on charcoal in the inner blowpipe flame. A brittle bead of metallic bismuth is thereby produced, and a lemon-yellow oxide, similar to lead-oxide, but darker, is deposited on the charcoal around. This deposit disappears when heated in the reducing flame, without colouring the outer flame, a character by which it is distinguished from lead. Oxide of bismuth is easily reduced on charcoal without addition of soda.

In *borax* on platinum-wire, bismuth-oxide dissolves to a clear glass, yellow while hot, and colourless when cold, if not supersaturated; in the latter case, yellowish-red while hot, yellow when cold. In the inner flame on charcoal, the borax-glass becomes grey and turbid, afterwards perfectly clear. The addition of *tin* makes it grey at first, but after complete reduction, colourless and transparent.

In *phosphorus-salt* on platinum-wire, a small quantity of bismuth-oxide forms a colourless glass; with a large quantity, the glass is yellow while hot, colourless, or sometimes enamel-white, on cooling. On charcoal, especially with addition of tin, the glass is transparent and colourless while hot, but becomes blackish-grey and opaque on cooling. (Berzelius and Plattner.)

Liquid Reactions.—The salts of bismuth are mostly colourless. They have an acid reaction, and their solutions when diluted with *water*, become milky, and yield a white precipitate, consisting of an insoluble basic salt, while an acid salt remains in solution. This reaction is best seen with the chloride, as the oxychloride formed is almost absolutely insoluble. *Iron*, *copper*, *lead*, and *tin*, precipitate bismuth from its solutions in the metallic state. *Sulphydric acid* and *sulphide of ammonium* throw down a brown-black precipitate of trisulphide of bismuth, insoluble in excess of sulphide of ammonium. *Caustic alkalis* and their *carbonates*, *phosphates*, *oxalates*, and *tartrates*, throw down white precipitates, insoluble in excess of caustic potash or soda. *Chromate of potassium* throws down a yellow precipitate of chromate of bismuth, insoluble in caustic potash. Soluble *sulphates* produce no precipitate. This last character, together with the insolubility of the precipitated chromate, hydrate, &c., in caustic potash, distinguishes bismuth from lead. From antimony, which resembles it in the decomposition of its salts by water, it is distinguished by its behaviour with sulphydric acid, and by the insolublility of the basic salts thrown down by water, in tartaric acid.

Quantitative Estimation.—The best reagent for precipitating bismuth from most of its solutions, is carbonate of ammonium, which, when added in excess, throws down the bismuth completely, provided the liquid be left to stand for some hours in a warm place. The precipitate, after being washed and dried, must be separated from the filter as completely as possible, the filter separately burned, and the precipitate ignited in a porcelain crucible; a platinum crucible would be attacked by it on ignition. It consists of trioxide of bismuth, Bi^2O^3, containing 89·66 per cent. of the metal.

If the solution contains hydrochloric acid, the bismuth cannot be estimated by precipitation with carbonate of ammonium or any other alkali, because the precipitate so formed would contain oxychloride of bismuth, and on igniting it, part of the bismuth would be volatilised as chloride. In this case, therefore, the bismuth must be precipitated by sulphydric acid, the sulphide of bismuth oxidised and dissolved by nitric acid, and the diluted solution precipitated by carbonate of ammonium.

Atomic Weight of Bismuth.—The first approximately correct determinations of the atomic weight of bismuth were made in 1815 by Lagerjhelm (Ann. Ch. xciv. 161), who, from the proportion of bismuth in the sulphide Bi^2S^3, in the oxide Bi^2O^3, and the sulphate $Bi^2(SO^4)^3$, estimated the atomic weight at 214·8, 212·8, and 212·3, respectively. L. Gmelin (Handbook, iv. 428) found that these numbers were too high, and that the oxide Bi^2O^3 contained at least 10·33 per cent. oxygen; whence

$$Bi^2 : O^3 = 89{\cdot}67 : 10{\cdot}33; \text{ and } Bi = \frac{89{\cdot}67 \times 48}{2 \times 10{\cdot}33} = 208{\cdot}2 \text{ at most.}$$

This result was confirmed by Schneider in 1851 (Pogg. Ann. lxxxii. 303). Pure bismuth was oxidised by nitric acid in a flask (the small portions of metal carried off by the vapours, being collected and allowed for), the solution evaporated, and the residue gently ignited. Eight experiments thus made, showed that 100 pts. of trioxide of bismuth, Bi^2O^3, contain from 10·318 to 10·366 pts. oxygen; mean = 10·345: whence $Bi = \frac{89·655}{20·690} \times 48 = 208·0$.

Lastly, Dumas (Ann. Ch. Pharm. cxiii. 38), has determined the atomic weight of bismuth by decomposing the trichloride $BiCl^3$ (prepared by passing chlorine gas over bismuth, and distilling till the product passed over is colourless), with excess of carbonate of sodium, and estimating the chlorine in the filtrate by means of a standard silver-solution. Three experiments, with the purest portion of the distillate, gave the numbers 209·88, 210·08, and 210·27. Dumas considers 210 to be the correct number.

Separation of Bismuth from other Elements.—From the *non-metallic* elements (excepting *selenium*), and from the *alkali-metals*, bismuth is separated by carbonate of ammonium; from the *earth-metals*, and from *iron*, *cobalt*, *nickel*, and the other metals of the second group (p. 217), it is separated by sulphydric acid; from *tin*, *arsenic*, *antimony*, and *tellurium*, by sulphide of ammonium; and from *copper* and *cadmium*, by ammonia. The separation of bismuth from *cadmium* may also be effected by cyanide of potassium, which dissolves the latter as cyanide of cadmium and potassium, and precipitates the bismuth. The precipitated bismuth, however, always contains potash, and must therefore be dissolved in nitric acid, and precipitated by carbonate of ammonium. Another mode of separating these two metals, given by Löwe (J. pr. Chem. lxvii. 464), is to heat the solution containing them with acid chromate of potassium, which throws down the bismuth as $Bi^2O^3.2Cr^2O^3$, and retains the cadmium in solution.

The separation of bismuth from *lead* cannot be effected by caustic potash, although lead is soluble in that reagent, and bismuth insoluble; for, when the metals are mixed in solution, the oxide of lead precipitated by potash always carries some bismuth-oxide down with it. The two metals may, however, be separated:—1. By sulphuric acid. The acid is to be added in excess, the solution evaporated till the excess of sulphuric acid begins to volatilise, and then diluted with water, whereupon the sulphate of lead is left undissolved, while the sulphate of bismuth dissolves completely, provided sufficient excess of sulphuric acid is present. The sulphate of lead is then collected on a filter, and washed with water containing sulphuric acid, and the bismuth is precipitated from the filtrate by carbonate of ammonium, after the excess of acid has been partly neutralised by ammonia. This method is not quite exact, because sulphate of lead is not perfectly insoluble in acid liquids; sulphuric acid, however, dissolves less of it than any other acid.—2. Another mode of separating lead from bismuth, is to dissolve the two metals or their oxides in nitric acid diluted with a very small quantity of water, then add hydrochloric acid in sufficient quantity to convert the metals into chlorides, and afterwards a considerable quantity of strong alcohol mixed with a little ether. The chloride of bismuth is thereby held in solution, while the chloride of lead is completely precipitated, and may be collected on a weighed filter, and washed with alcohol containing ether. Lastly, the alcoholic solution of chloride of bismuth is diluted with water, the alcohol evaporated, and the bismuth precipitated by sulphuretted hydrogen. This method becomes more exact as the alcohol used is stronger.—3. Ullgren separates bismuth from lead by precipitating the two metals as carbonates, redissolving them in acetic acid, and immersing in the liquid a weighed strip of clean sheet-lead, which must be completely covered by the liquid; the vessel is then closed and left to itself for several hours. The bismuth is thereby precipitated as a metallic powder. It is rinsed off the surface of the lead, which is then dried and weighed, and the precipitated bismuth is collected, dissolved in nitric acid, and precipitated by carbonate of ammonium, or estimated by simply evaporating the solution and igniting the residue. The lead in the solution is also precipitated by carbonate of ammonium, and the carbonate of lead is converted into oxide by ignition, and weighed, a deduction being made of the quantity of lead-oxide corresponding to the lead which has been dissolved.—4. When lead and bismuth are mixed in the metallic state, they may be separated by passing chlorine over the heated alloy, chloride of bismuth then volatilising, while chloride of lead remains. Great care is, however, required in regulating the heat, as too high a temperature would volatilise some of the chloride of lead, and if the heat be too low, a portion of the chloride of bismuth will remain.

For the separation of bismuth from *mercury*, *silver*, *gold*, *platinum*, and its allied metals, see the several metals.

Valuation of Bismuth-ores.—Ores containing only metallic bismuth, are assayed by heating them in a crucible perforated at the bottom, and standing over a receiver, into which the melted metal runs. The process is not quite exact, as a small quantity of the metal remains mixed with the ore; but it is sufficient for a check on the results of the smelting on the large scale. If the ore likewise contains sulphide of bismuth, it is ignited with two or three times its weight of black flux, sometimes with addition of metallic iron, also of borax, if much earthy matter is present. If the ore also contains other metals, which are reduced together with the bismuth, the metallic button must be dissolved, and the several metals separated by analysis in the wet way, as above described. (Kerl, Hüttenkunde, ii. 355.)

BISMUTH, FLUORIDE OF. Soluble in water and deposited as a white powder, when the aqueous solution is evaporated. (Berzelius.)

BISMUTH, IODIDE OF. BiI^3.—Obtained by mixing 1 at. of trisulphide of bismuth (which has been prepared by precipitation) with 3 at. of iodine, and gently heating the mixture in a capacious loosely covered glass globe, on the sides of which the compound condenses. The iodine simply takes the place of the sulphur (Schneider.) It is likewise produced by throwing iodine in small portions into a tube in which bismuth is strongly heated, and distilling out of contact with the air (Weber). It forms large brilliant grey hexagonal tables, which, according to Nicklès (Compt. rend. l. 872) are isomorphous with the tri-iodides of arsenic and antimony. Metallic bismuth decomposes it in the same manner as the tribromide. (Weber).

An *oxyiodide* of bismuth, BiIO, is formed when the tri-iodide is heated for some time in a crucible, and collects below the crystallised iodide thus obtained, in a mass of copper-coloured rhombic laminæ. In a close vessel, it may be partially volatilised without alteration, but when strongly heated in contact with the air, it is converted into oxide. It is not decomposed by water or by alkaline solutions; hydrochloric acid dissolves it without alteration; nitric acid decomposes it, with separation of iodine. (Schneider, J. pr. Chem. lxxix. 424.)

A *sulphiodide*, BiIS, is obtained by adding to melted iodide of bismuth, as much sulphur as it is capable of dissolving; it is likewise produced in the preparation of the tri-iodide by Schneider's method, and collects at the bottom of the vessel, together with a small quantity of the iodide, in small, shining, steel-grey needles. It appears to have the same form as the trisulphide. (Schneider, J. pr. Chem. lxxix. 422.)

E. A.

BISMUTH, OXIDES OF. Bismuth forms two definite compounds with oxygen, *Bismuthous oxide* or *trioxide of bismuth*, Bi^2O^3, and *bismuthic oxide* or *anhydride*, Bi^2O^5. An intermediate oxide, Bi^2O^4, is known, but it may be regarded as a compound of the other two—a *bismuthate of bismuth*, $Bi^2O^3 . Bi^2O^5$. A dioxide, Bi^2O^2, appears also to exist; it is formed when a solution of a bismuth-salt is treated with protochloride of tin. A corresponding sulphide is known.

BISMUTHOUS OXIDE, or TRIOXIDE OF BISMUTH, Bi^2O^3, is formed when the metal is roasted in air, but is best obtained by gently igniting the subnitrate. It is a pale yellow powder, which melts at a red heat, and solidifies on cooling to a glass having a deeper yellow tint. It occurs native, as *bismuth-ochre*, associated with iron and some other impurities (Bi^2O^3 86·4 per cent.; Fe^4O^3 5·1; CO^2 4·1; water 3·4), at Schneeberg in Saxony, at Joachimsthal in Bohemia, and with native gold at Beresof in Siberia. (Dana, ii. 141.)

The hydrated oxide of bismuth, $BiHO^2$. or $Bi^2O^3H^2O$, is obtained as a white precipitate when a solution of subnitrate of bismuth is decomposed by an alkali. If the hydrate be boiled with potash, it loses water, and is changed into a yellow crystalline powder which is the anhydrous oxide.

The hydrate is occasionally used in analysis for converting into oxides certain metallic sulphides soluble in alkalis. For this purpose, the alkaline solutions are boiled with the hydrated oxide.

Both the hydrate and the anhydrous oxide dissolve in the stronger acids, forming the normal bismuth salts, which have the composition $Bi'''A^3$, the symbol A denoting an acid radicle, *e. g.*:

$$BiCl^3;\ Bi(NO^3)^3 = \left.\begin{matrix}(NO^2)^3\\ Bi'''\end{matrix}\right\}O^3;\ Bi^2(SO^4)^3 = \left.\begin{matrix}(SO''^2)^3\\ (Bi''')^2\end{matrix}\right\}O^6, \&c.$$

Many of these salts crystallise well, but cannot exist in solution unless an excess of acid is present. On diluting the solutions with water, a basic salt is precipitated, and an acid salt remains in solution.

BISMUTHIC OXIDE OR ANHYDRIDE, Bi^2O^5;—in combination: BISMUTHIC ACID.—Prepared by passing chlorine through a concentrated solution of potash which contains hydrated trioxide of bismuth in suspension. A blood-red substance then separates, which is a mixture of hydrated bismuthic acid, and trioxide of bismuth. This is treated with dilute nitric acid, which dissolves the oxide, but, in the cold, does not attack the acid.

Bismuthic oxide is a bright red powder, which loses part of its oxygen at a temperature little above 100° C. and becomes converted into the intermediate oxide, Bi^2O^4, bismuthate of bismuth. Acids also decompose it, reducing it to the state of bismuthous oxide, which then combines with the acid.

The bismuthates are little known, and of no importance; according to Arppe, bismuthic acid forms with potash, a salt which is an *acid bismuthate of potassium:* $Bi^2KHO^4 = BiKO^3.BiHO^3$. E. A.

BISMUTH, OXYCHLORIDE OF. (p. 591.)

BISMUTH OXYGEN-SALTS OF. See the several acids.

BISMUTH, PHOSPHIDE OF. Melted bismuth takes up a small quantity of phosphorus, being thereby rendered more brittle and less laminar. Phosphoretted hydrogen gas throws down from solution of nitrate of bismuth a black phosphide of the metal, which gives off all its phosphorus by distillation. (Berzelius.)

BISMUTH, SELENIDE OF. Bismuth and selenium unite when heated together with faint evolution of light and heat, and form a silver-white mass, having a crystalline fracture, and fusing at a red heat: the fused mass has a specular surface. (Berzelius.)

BISMUTH, SULPHIDES OF. Bismuth readily unites with *sulphur*. When the two substances in fine powder are fused together, they combine, with disengagement of heat. Two distinct compounds are known.

Disulphide of Bismuth, $Bi''S$.—According to Wertheim, it is obtained crystallised by melting together bismuth and trisulphide of bismuth in equivalent quantities. The mixture is then allowed to cool slowly, on which the sulphide crystallises from the liquid metal, which may be poured off from the crystals. More recently it has been shown that these crystals, although giving by analysis numbers corresponding to BiS, are really a compound of trisulphide of bismuth with metallic bismuth. According to Schneider, disulphide of bismuth may be prepared in the moist way, by mixing an alkaline solution of bismuthous oxide with an alkaline solution of stannous oxide, and precipitating with sulphuretted hydrogen. The tin remains dissolved, and a black precipitate is formed, which, when washed and dried in the water-bath, is found to have the composition $BiS.H^2O$. It is a black lustreless powder, which, under the burnisher, takes the form of black laminæ.

Trisulphide of Bismuth, Bi^2S^3, occurs native as bismuth-glance, or *bismuthine*, in Cumberland and Cornwall, also in Saxony, at Bastnäs in Sweden, and according to Shepard, at Haddam in Connecticut, associated with chrysoberyl. It crystallises in acicular prisms of the trimetric system, isomorphous with native sulphide of antimony. $\infty\bar{P} \,.\, \infty\breve{P}\infty \,.\, \infty P\infty \,.\, \infty P3 \,.\, oP$. Inclination of $\infty P : \infty P = 91° 30'$. Cleavage perfect parallel to oP and $\infty\breve{P}\infty$; less perfect parallel to $\infty\bar{P}\infty$. It occurs also massive, with foliated or fibrous structure. Specific gravity 6·4 to 6·55. Hardness = 2 to 2·5. Opaque, with metallic lustre, lead-grey colour and streak. Sectile. (Dana, ii. 33.)

The same compound is prepared in the dry way, by fusing pulverised bismuth with one-third of its weight of sulphur, and removing the excess of sulphur by a second fusion. A laminated mass is thus obtained, composed of crystals having the same form as the native sulphide. According to Marx, it expands to the amount of one-fourth its volume in solidifying. The trisulphide is also obtained as a brown-black precipitate, when sulphydric acid gas is passed into the solution of a bismuth-salt. E. A.

BISMUTH, SULPHOCHLORIDE OF. BiSCl, or $BiCl^3.Bi^2S^3$.—This compound is best obtained by gradually adding pulverised trisulphide of bismuth to melted ammonio-bismuthous chloride ($2NH^4Cl.BiCl^3$), and washing the resulting mass with water acidulated with hydrochloric acid. It is also formed by heating the same double chloride with sulphur, or in sulphydric acid gas. It forms small, metallic-shining, blue-grey crystalline needles, which yield a red powder. Heated in carbonic acid gas, it gives off chloride of bismuth and leaves the sulphide; heated in hydrogen, it gives off hydrochloric and sulphydric acids, and leaves bismuth. It is decomposed by strong hydrochloric and strong nitric acid; also by alkalis, which remove the chlorine and leave an oxysulphide. (R. Schneider, Pogg. Ann. xciii. 464.)

BISMUTH, TELLURIC. Bi^2STe. See Tellurium.

BISMUTH, TELLURIDE OF. The two metals unite in all proportions by fusion.

BISMUTH-BLENDE. Native silicate of bismuth. See Silicates.

BISMUTH-GLANCE, or **BISMUTHINE.** Native trisulphide of bismuth (see above).

BISMUTH-NICKEL. *Grünauite. Saynite.*—A sulphide of bismuth and nickel, found, together with quartz and copper pyrites, at Grünau in Sayn Altenkirchen, crystallised in regular octahedrons, sometimes perfect, sometimes having the summits more or less replaced by faces of the cube. Cleavage octahedral. Specific gravity 5·13. Hardness 4·5. Colour, light steel-grey to silver-white, often yellowish or greyish from tarnish. Its composition in 100 parts is given by the following analyses:

S	Bi	Ni	Fe	Co	Cu	Pb	
38·46	14·11	40·65	3·48	0·28	1·68	1·58	Kobell.
31·99	10·49	22·03	5·55	11·24	11·59	7·11	Schnabel.
33·10	10·41	22·78	6·06	11·73	11·56	4·36	„

Before the blowpipe it melts to a grey, brittle, magnetic globule, colouring the charcoal greenish-yellow. Dissolves in nitric acid, excepting the sulphur. (Dana, ii. 44.)

BISMUTH-OCHRE. Native trioxide of bismuth (p. 594).

BISMUTH-RADICLES, ORGANIC. The only compounds of this class as yet obtained, are the *Bismuthides of Ethyl*, viz. *Bistriethyl*, discovered by Löwig and Schweizer (Ann. Ch. Pharm. lxxv. 355), and further examined by Breed (*ibid.* lxxxii. 106), and *Bisethyl*, discovered by Dünhaupt in 1854 (*ibid.* xcii. 372).

BISETHYL. C^2H^5Bi.—The *chloride* of this radicle, $C^2H^5BiCl^2$ (?) is obtained, together with a precipitate of chloride of hydrargethyl, by the action of bistriethyl on chloride of mercury (p. 596). The chloride of bisethyl remains in solution and may be obtained by spontaneous evaporation in crystals, which however do not dissolve completely in water, but leave a white powder. On adding iodide of potassium to the aqueous solution, then diluting with water till turbidity is produced, boiling till the solution becomes clear, and leaving it to cool, *iodide of bisethyl* separates in yellow six-sided laminæ, which appear to have the composition $C^2H^5BiI^2$. A solution of this compound in hydrated alcohol treated with ammonia, forms a yellowish-white precipitate of the *hydrated oxide*, which, after drying in vacuo, ignites spontaneously in the air, giving off a dense yellow vapour. The oxide appears also to be formed by the spontaneous oxidation of bistriethyl, 2 atoms of ethyl being eliminated. *Sulphide of bisethyl* is formed by treating the iodide with sulphydric acid; and the nitrate and sulphate by acting on the iodide with the corresponding silver-salts. (Dünhaupt.)

BISTRIETHYL, or TRIETHYL-BISMUTHINE. $(C^2H^5)^3Bi$. *Bismethyl.*—Formed by the action of iodide of ethyl on bismuthide of potassium.

Preparation.—Bismuthide of potassium, finely pounded, and without admixture of sand, is introduced into a small flask; iodide of ethyl added in excess; the flask closed, and immediately connected with a long narrow distillation-tube passing into a receiver surrounded with ice, all these manipulations being performed as quickly as possible. In a few minutes, the action begins, the mixture becomes heated, and the excess of iodide of ethyl distils over. Water free from air is then introduced into the flask, which is immediately closed and heated in the water-bath, till the mass becomes soft and the iodide of potassium is dissolved. The same operations are repeated with a considerable number of flasks; the disintegrated contents transferred as quickly as possible into a large flask filled with carbonic anhydride; shaken up several times with a large quantity of ether; the ethereal solution mixed with the de-aërated water; and the ether completely distilled off in the water-bath. The bistriethyl remains at the bottom of the water, and is purified by distilling it with water (it cannot be distilled alone, without decomposition), shaking it up with a small quantity of dilute nitric acid to free it from oxide, and drying over chloride of calcium. During all these operations, the air must be carefully excluded (Breed). 3 lbs. of bismuthide of potassium and 1 lb. of iodide of ethyl, yield 4 or 5 oz. of pure bistriethyl. (Dünhaupt.)

Properties.—Transparent, very mobile liquid, sometimes colourless, but often slightly tinged with yellow. Has an unpleasant odour like that of stibtriethyl, and its vapour, when inhaled, even in small quantity, produces a very disagreeable burning sensation on the tip of the tongue (Breed). Insoluble in water, sparingly soluble in ether, readily in absolute alcohol.

Decompositions.—1. Bistriethyl heated in a retort, begins to boil at about 50° C., giving off a gas free from bismuth, which burns with a clear flame, while metallic bismuth separates out in the retort. If the heat be continued, the thermometer rises above 160° C., and continues to rise till a sudden and violent explosion takes place, which shatters the apparatus (Breed). The dilute ethereal solution is also decomposed when left to evaporate in the air, leaving a white residue of hydrated oxide of bismuth (Dünhaupt).—2. Bistriethyl exposed to the air, gives off thick yellow vapours and takes fire with slight explosion, diffusing a dense yellow smoke of bismuth-oxide; this effect is best shown by moistening a piece of filtering paper with the liquid and exposing it to the air.—3. Fuming nitric acid decomposes bistriethyl, with explosion and vivid combustion.—4. Bistriethyl burns in chlorine gas with separation of charcoal, and takes fire in contact with bromine. In general, its reactions resemble those of stibtriethyl (Breed).—5. Bistriethyl added to solutions of metallic salts (*e.g.* to nitrate of silver or corrosive sublimate), does not simply throw down the oxide, but is itself decomposed. On adding an alcoholic solution of bistriethyl to a not too dilute solution of protochloride of mercury, the former being poured slowly and with constant stirring into the latter, a very large precipitate of mercurous chloride is immediately obtained, chloride of bismuth and hydrochloric ether being doubtless formed at the same time. But if the process be reversed, and a hot dilute alcoholic solution of corrosive sublimate be poured in a thin stream and with constant stirring into a dilute alcoholic solution of bistriethyl to which a few drops of hydrochloric acid have been added, to prevent separation of oxide of bismuth, no precipitate is formed at first; but after some time, a bulky precipitate appears, which however is again completely dissolved if the liquid be heated. The reaction is terminated when a drop of the liquid no longer produces a white precipitate in a solution of corrosive sublimate; by a little care, it may be arranged that neither liquid shall predominate. If the liquid be then heated on the water-bath till it becomes perfectly clear, separated, if necessary, from a small quantity of metallic mercury by decantation, and then left to cool, light, crystalline, silvery, iridescent laminæ separate out and gradually fill the whole fluid. These crystals consist of *chloride of hydrargethyl*, $C^2H^5Hg^2Cl$; the solution from which they are deposited contains *chloride of bisethyl*, $C^2H^5BiCl^2$ (Dünhaupt):

$$(C^2H^5)^3Bi + 4HgCl = 2C^2H^5Hg^2Cl + C^2H^5BiCl^2.$$

Combinations.—Bistriethyl combines with *Bromine*, *Iodine*, *Sulphur*, &c.; but the compounds are less stable than those of stibtriethyl.

Bromide of Bistriethyl appears to be formed when bromine is added to an alcoholic solution of bistriethyl; but the solution deposits bismuth when evaporated.

Iodide of Bistriethyl.—When iodine is added to an alcoholic solution of bistriethyl, heat is evolved, the colour of the iodine disappears, and iodide of bistriethyl is formed. This compound is less stable than iodide of stibtriethyl; when its alcoholic solution is left to itself for a while, iodide of bismuth separates out. (Breed.)

An iodide having the composition $C^6H^{15}Bi^3I^5$, or $(C^2H^5)^3BiI^2.Bi^2I^3$, is obtained by adding iodine to a tolerably strong alcoholic solution of bistriethyl, till its colour [no longer?] disappears, filtering from the precipitate, and adding to the filtrate a large quantity of water at 40° C. A small quantity of a ruby-coloured liquid separates; and if the watery liquid be poured off from this, a large quantity of beautiful red needle-shaped crystals are formed as it cools; these must be immediately collected and dried in vacuo. The same compound is formed when bistriethyl is left for a considerable time in contact with dilute nitric acid and then mixed with iodide of potassium. It is sparingly soluble in water, but dissolves pretty readily in alcohol and ether; the solutions have a pale yellow colour. The compound heated on platinum foil gives off a strong yellow vapour which takes fire on coming in contact with flame. (Dünhaupt.)

Another iodine-compound, having the formula $(C^2H^5)^4Bi.2C^2H^5I$, is contained in the above-mentioned ruby-coloured liquid; but it is very instable. (Dünhaupt.)

Sulphide of Bistriethyl, has not been obtained in the separate state. Bistriethyl which has been long exposed to the air under water, gives with sulphuretted hydrogen, first a yellow, then a brown precipitate, consisting of $(C^2H^5)^3BiS.Bi^2S^3$. (Dünhaupt.)

BISMUTH-SILVER. A mineral sometimes occurring in acicular or capillary crystallisations, but more generally amorphous, as at Schapbach in Baden; it is found also in the cupreous shale of Mansfeld, Thuringia. It is soft and sectile, opaque, with metallic lustre and tin-white or greyish colour, subject to tarnish; fracture uneven. Contains, according to Klaproth's analysis, 27 per cent. bismuth, 33 lead, 15 silver, 4·3 iron, 0·9 copper, and 16·3 sulphur. A *bismuth-silver* from the mine of San Antonio near Copaipo, Chili, was found by Domeyko to contain 60·1 per cent. silver, 10·1 bismuth, 7·8 copper, 2·8 arsenic, and 19·2 gangue. It occurs disseminated, and has one or more imperfect cleavages, and is probably either monometric or rhombohedral. (Dana, ii. 16.)

BISMUTITE. Native carbonate of bismuth. See CARBONATES.

BISSA-BOL. A gum resin from Arabia, resembling myrrh. (Vaughan, Pharm. J. Trans. xii. 227.)

BISTRE. A brown pigment, consisting of the finer parts of wood-soot, separated from the grosser by washing. The soot of beech-wood is said to yield the best bistre. (See *Ure's Dictionary of Arts, Manufactures, and Mines*, i. 307.)

BITTER-ALMOND OIL. A peculiar volatile oil obtained by distilling bitter-almonds with water. It was discovered by Martrès in 1803; Stange showed that the crystallised acid which is produced from it is benzoic acid; Robiquet, and Liebig and Wöhler explained its formation; and Liebig and Wöhler (1832, Ann. Ch. Pharm. xxii. 1) first fully examined it. It is also obtained from the amygdaliferous parts of most *Pomeæ* and *Amygdaleæ;* from the leaves of the cherry-laurel (*Cerasus lauro-cerasus*), and of *Cerasus padus*, from peach and cherry-kernels, &c. It is possible that many of these oils are not identical, but isomeric, with bitter-almond oil, and that it is owing to their presence that different specimens of the commercial oil yield with the same reagent such different results. The chief constituent of the oil is hydride of benzoyl, always accompanied by hydrocyanic acid and other compounds (see BENZOYL, HYDRIDE OF). The oil does not exist ready-formed in bitter-almonds, but is produced by the action of water and a peculiar ferment, *emulsin* or *synaptase*, upon the amygdalin contained in the almonds, which is thereby converted into hydride of benzoyl, hydrocyanic acid, and glucose:

$$\underset{\text{Amygdalin.}}{C^{20}H^{27}NO^{11}} + 2H^2O = \underset{\substack{\text{Hydride}\\ \text{of benzoyl.}}}{C^7H^6O} + CNH + \underset{\text{Glucose.}}{2C^6H^{12}O^6}.$$

The oil is thus prepared: Bitter-almonds are crushed, and freed from fixed oil by cold pressing, then stirred up to a thin paste with 4—6 pts. cold or lukewarm water, and the mixture allowed to stand for twenty-four hours before distillation. If distilled over the open fire, it is very apt to froth over, unless it is stirred continually; for this reason it is best distilled with vapour of water. This may be done by covering the bottom of the still with a thick layer of coarse sand saturated with water, and pouring the almond-paste upon it. The frothing may also be avoided by removing most of the solid matter before distilling. The first portion of the distillate is richest in oil, and in hydrocyanic acid also, and is therefore clear; the latter portions, containing less hydrocyanic acid, are milky. The distillation is continued as long as the liquid which comes over smells of bitter-almonds; the oil in the receiver is then separated from the water, which, as it contains a good deal of oil in solution, is again distilled, when the oil passes over with the first portions of the water. The addition of chloride of sodium facilitates the separation of the oil. 1000 pts. almonds do not yield more than 7 or 8 pts. oil.

Bitter-almond oil is colourless when freshly prepared, but soon becomes yellow; it has a peculiar strong aromatic smell, besides that of prussic acid, and a burning taste; is heavier than water; boils at about 180° C., and burns with a smoky flame. Its poisonous action is entirely owing to the presence of prussic acid. (For methods of purifying the oil, see BENZOYL, HYDRIDE OF.)

Bitter-almond oil was formerly much used in perfumery, but it is now replaced in great measure by nitrobenzene (*essence de Mirbane*). Being an expensive article, it is very liable to adulteration, usually with alcohol (which, if added in moderation, does not materially affect its smell), light ethereal oils, or nitrobenzene. Light oils, whose smell is masked by that of hydride of benzoyl, may be detected by allowing the latter to oxidise into benzoic acid by exposure to the air, when the smell of the former becomes evident, or by their effect on the specific gravity of the oil, a method which applies to alcohol also. Alcohol may also be detected by agitating the oil with twice its volume of nitric acid of specific gravity 1·42; with unadulterated oil, no immediate action is produced; but, if 8—10 per cent. alcohol be present, red fumes are given off with effervescence. By using acid of 1·5 specific gravity, as little as 3—4 per cent. alcohol may be detected (Redwood). A good reagent for detecting adulterations is a strong solution of an acid sulphite of alkali-metal, which dissolves the pure oil entirely, but leaves behind all impurities which are not of the nature of aldehydes.

Owing principally to the presence of hydrocyanic acid, bitter-almond oil behaves with several reagents differently from hydride of benzoyl. By *heat* and by oxidising agents generally, *e.g.* by nitric acid, it is acted on in the same manner as hydride of benzoyl. With *sulphuric acid*, it yields stilbous acid, and (perhaps) benzoate of hydride of benzoyl. A mixture of Nordhausen sulphuric acid with bitter-almond oil yields, on addition of water, a crystalline body, which presents the properties of mandelic acid. Dry *chlorine* acts upon it as upon hydride of benzoyl; with moist chlorine it forms stilbesic acid and *benzoate of hydride of benzoyl*. To this latter compound, which is frequently regarded as identical with stilbous acid, Liebig assigns the formula $C^{21}H^{18}O^4 = 2C^7H^6O + C^7H^6O^2$. Bitter-almond oil saturated with moist chlorine solidifies finally to a crystalline mass, which, when washed with cold ether, leaves this compound as a crystalline powder. It is insoluble in water, slightly soluble in cold ether, abundantly in alcohol. When heated, it melts and volatilises undecomposed. Heated with alcoholic potash, it yields potassic benzoate. With *hydrochloric acid*, it yields either hydrocyanate of hydride of benzoyl or mandelic acid. With *chloride of* *sulphur*, it yields stilbous acid. With *sulphide of ammonium*, it yields hydride of thiobenzoyl, hydride of sulphozobenzoyl, and sulphydrate of azobenzoyl. With *bisulphide of carbon* and *ammonia*, it yields sulphocyanobenzylene. With *cyanide of potassium*, it yields sometimes benzoin, sometimes benzamide. Solid *potash* converts it into benzoic acid; aqueous or alcoholic potash (especially the latter) into benzoin. With *ammonia*, it yields very various products, according to circumstances; these are azobenzoide, azobenzoidin, azobenzoyl, benzamil, benzhydramide, benzoylazotide, dibenzoylimide, hydrobenzamide, stilbazide. Most of these compounds were discovered by Laurent, and many are very imperfectly known. *Baryta-* or *lime-water* converts it into benzoin. F. T. C.

BITTER-ALMOND WATER. A pharmaceutical preparation, employed in medicine, consisting of a solution of bitter-almond oil in water. It is prepared in the same manner as bitter-almond oil; but, since the water must be of a known strength, the quantity of almonds and water to be employed and of distillate to be collected is fixed by the pharmacopœia. These quantities vary in different pharmacopœias: in the Prussian, 2 lbs. almonds are pressed and macerated with 10 lbs. water, 4 ozs. alcohol added, and 2 lbs. of distillate collected. The Parisian pharmacopœia collects 2 lbs. the Saxon 3 lbs. of distillate for each pound of almonds. The addition of alcohol does not seem to have any advantage. Heat must be carefully avoided in the pressure and maceration of the almonds. Bitter-almond water is generally a more or less milky liquid, smelling and tasting strongly of crude bitter-almond oil; it decomposes by exposure to the air, and must therefore be kept in stoppered bottles completely full. Its strength is very uncertain, however closely the pharmacopœia directions are adhered to. It is usually valued by the amount of prussic acid which it contains, which may be readily determined by Liebig's volumetric method (see HYDROCYANIC ACID, under CYANOGEN); the Prussian pharmacopœia requires it to contain 0·14 per cent. prussic acid. *Laurel-water*, prepared from laurel leaves, and *cherry-water* from wild cherries, contain the same constituents as bitter-almond water. The latter may be distinguished from laurel-water by becoming milky immediately on addition of ammonia, an effect which is not produced on laurel-water till after some time; or, according to Lepage, by chloride of gold, which gives with both waters a yellow colour, which, in bitter-almond water, disappears in eight hours, while in laurel-water it remains for twenty-four hours. (J. Ch. méd. xxiv. 365.) F. T. C.

BITTER PRINCIPLE. Many vegetable substances yield bitter extracts, which were formerly supposed to contain a common constituent, called *Principium amarum*. More exact investigation having shown, however, that many of these vegetable bitters are definite chemical compounds of very various composition, *e.g.* picric acid and the vegetable alkaloids, the term bitter principle is now restricted to the brown amorphous bitter extractive matter obtained from many plants by boiling with water, evaporating the extract to dryness, exhausting with hydrated alcohol, evaporating, and treating the residue with absolute alcohol, which dissolves resins, &c., and leaves the bitter substance undissolved. The products thus obtained, are not, generally speaking, of definite constitution. From some plants, however, more definite bitter principles are obtained, *e. g. absinthin* from wormwood, *aloin* from aloes, &c.

BITTERN. The mother-water which remains after the crystallisation of common salt from sea-water or the water of salt-springs. It contains a considerable quantity of sulphate and chloride of magnesium, to which its bitterness is owing, also more or less bromine and iodine.

BITTER SPAR or **RHOMBSPAR.** *Brown-spar. Pearl-spar. Talc-spar. Dolomite. Chaux carbonatée magnésifère.*—This mineral crystallises in rhombohedrons, which were formerly confounded with those of calcspar, but differ in the angles, the primary form being an acute rhombohedron of 106° 18′, and 73° 42′ (mean). The crystals are generally rhombohedrons R, with more acute or more obtuse rhombohedron in combination, the base 0R and the hexagonal prisms ∞R often occurring. The rhomb R generally has its faces curved like a saddle; $\frac{1}{2}R$ is more generally lenticular. Cleavage parallel to R. Fracture conchoïdal, uneven, splintery, and earthy. Colour white, greyish, or yellow, with a somewhat pearly lustre. Rarely transparent, but exhibits various degrees of translucence down to complete opacity. Hardness 3·5 to 4·5. Specific gravity 2·8 to 3·0. Its formula is $(Ca^2; Mg^2)CO^3$, the calcium and magnesium replacing one another in any proportion, so that it presents all varieties of composition, from that of calcspar to that of magnesite. Iron (*ferrosum*) and manganese (*manganosum*) also occur, replacing the other metals in subordinate proportions. In the state of powder, it dissolves readily in warm hydrochloric acid, but in lumps the acid scarcely acts upon it. Before the blowpipe, it becomes caustic, but does not melt. It is usually imbedded in serpentine, chlorite, or steatite, and is found in the Tyrol, Salzburg, and Dauphiny; in Scotland, on the borders of Loch Lomond, in chlorite slate, and near Newton Stewart in Galloway, also in the Isle of Man. It bears the same relation to dolomite, or massive magnesian limestone, that calcspar bears to common limestone.

BITTERSWEET. *Stipites Dulcamara.* The stems of *Solanum Dulcamara* (*q.v.*)

BITUMEN. This term includes a considerable number of inflammable mineral substances, mainly consisting of hydrocarbons. They are of various consistence, from thin fluid to solid, but the solid bitumens are for the most part liquefiable at a moderate heat. The purest kind of fluid bitumen, called *Naphtha*, or *Rock-oil*, is a colourless liquid of specific gravity 0·7 to 0·84, and with a bituminous odour. It often occurs in nature combined with asphalt and other solid bitumens. *Petroleum* is a dark-coloured, fluid variety containing much naphtha. *Maltha* or *mineral tar* is a more viscid variety. The solid bitumens are *Asphalt*, already described (p. 425), *Mineral tallow*, or *Hatchetin*, and *Elastic bitumen*, *Mineral Caoutchouc* or *Elaterite*. (See the several substances in alphabetical order. For the practical uses of bitumen, see *Ure's Dictionary of Arts, Manufactures and Mines*, i. 308.)

BIURET. $C^2H^5N^3O^2$ (dried at 100° C.); $C^2H^5N^3O^2.H^2O$ (crystallised).—A product of the decomposition of urea and nitrate of urea. It is isomeric with acid cyanate of ammonium, $2CHNO.NH^3$, and may be regarded as a secondary amide, $N\left\{\begin{matrix}(CH^2NO)^2\\H\end{matrix}\right.$, whereas urea is a primary amide containing the same radicle, $N\left\{\begin{matrix}CH^2NO\\H^2\end{matrix}\right.$, and isomeric with neutral cyanate of ammonium, $CHNO.NH^3$.

The formation of biuret from urea is represented by the equation

$$\underbrace{2CH^4N^2O}_{\text{Urea.}} = \underbrace{C^2H^5N^3O^2}_{\text{Biuret.}} + NH^3.$$

To prepare it, urea is melted in an oil-bath for some time at 150° to 170° C.; and as soon as the evolution of ammonia ceases and the residue becomes pasty, this residue is treated with a very small quantity of boiling water; the liquid, after filtration, is precipitated by a solution of subacetate of lead; the precipitate, consisting of cyanurate and ammelidate of lead, is separated by filtration; and the liquid, after being treated with sulphuretted hydrogen to remove the excess of lead, and again filtered, is evaporated till it crystallises. Biuret is then deposited in small granular crystals, which may be purified by recrystallisation from water. It is also obtained, though in small quantity, by the action of heat upon nitrate of urea.

Biuret dissolves very easily in water and in alcohol, and crystallises from the latter liquid in long anhydrous leafy crystals, and from water in hydrated crystals, which give off their water of crystallisation when exposed to dry air or dried at 100° C. It dissolves without decomposition in cold strong sulphuric acid, and is not altered by boiling with nitric acid, unless the acid is very strong. Its solution is not precipitated by lead or silver salts, by gallic acid, or by tannin. On adding a few drops of a solution of copper salt to a solution of biuret, and then a slight excess of potash, a deep red colour is produced. This reaction takes place also with solutions of biuret in acids or in ammonia, and affords a very delicate test of its presence. Biuret when heated, melts, gives off vapours of ammonia, and ultimately leaves pure cyanuric acid:

$$3C^2H^5N^3O^2 = 2C^3H^3N^3O^3 + 3NH^3.$$

(Wiedemann, Pogg. Ann. lxxiv. 67.)

BIXIN. A colouring matter contained in annotto (the red paste obtained by crushing the seeds of the *Bixa orellana*). According to Chevreul, annotto contains two colouring matters, viz. *orellin*, a yellow dye, soluble in water and alcohol, but sparingly in ether, and *bixin*, an orange-coloured dye, sparingly soluble in water, easily in alcohol and ether. According to Kerndt, bixin is $C^{16}H^{20}O^3$, and when exposed to the air, and in the moist state, is partly converted into orellin. According to Preisser, Ann. Ch. Pharm. lii. 382), bixin is obtained in small slightly yellowish crystals, by treating lumps of pure annotto with carbonate of sodium, precipitating with basic nitrate of lead, decomposing the precipitate with sulphuretted hydrogen, and evaporating the colourless filtrate. It is bitter, soluble in water, alcohol, and ether, volatile when heated, turned yellow by sulphuric and nitric acids, orange-yellow by chromic acid. Treated with ammonia in contact with the air, it is converted into a dark red-brown substance, *bixein*, which is the red-colouring matter of annotto. It combines with lead-oxide and alkalis, and is turned blue by sulphuric acid. (Preisser.)

According to Girardin (J. Pharm. [3] xxi. 174), the name of bixin is applied commercially to a variety of annotto, having six to ten times the colouring power of common annotto, a superiority which it appears to owe to a quicker process of extraction.

BLACK BAND. A variety of carbonate of iron. See IRON and CARBONATES.

BLACK CHALK. This mineral has a bluish-black colour, a slaty texture, soils the fingers, and is meagre to the touch. It contains about 64 silica, 11 alumina, 11 carbon, with a little iron and water. It is found in primitive mountains, and also sometimes near coal formations. It occurs in Caernarvonshire and in the island of Isla.

BLACK JACK. The miners distinguish blende, or mock lead, by this name. It is an ore of zinc.

BLACK LEAD. See GRAPHITE and PLUMBAGO.

BLACK WADD. One of the ores of manganese.

BLANCHININE. The name of an alkaloid said to exist in *China blanca.*

BLANQUETTE. A kind of crude soda, less powerful than barilla, obtained at Aigues-Mortes, by the incineration of *Salsola Tragus* and *S. Kali.*

BLAPS OBTUSA. This insect contains, according to Hornung and Bley (J. pr. Chem. vi. 237), a red colouring matter, fatty and volatile oil, resin, formic acid, uric acid, chitin, wax, and other constituents.

BLEACHING. The chemical art by which the various articles used for clothing are deprived of their natural dark colour and rendered white.

The oldest method of bleaching, which is still practised in some localities, and for particular kinds of goods, especially for hempen and flaxen goods, consists in extending the tissues on the grass of a meadow, so as to expose them for some days to the united action of light, air, and water, then washing them in alkaline ley, and repeating this series of operations a considerable number of times.

This mode of bleaching is effective, but slow, and involves a great amount of labour. About 1785, Berthollet proposed the use of chlorine for bleaching vegetable tissues; but its introduction met with considerable opposition from manufacturers, because the mode of applying it being but imperfectly understood, its action was uncertain, and moreover it was found to injure the tissues; gradually, however, these difficulties have been overcome, and the use of chlorine for bleaching cotton goods has entirely superseded the old method. Chlorine was first used in the form of aqueous solution; afterwards solutions of chlorine in caustic alkalis, that is to say, solutions of hypochlorite of potassium or sodium, the so-called chlorides of potash and soda, were used; but these compounds are now almost entirely superseded by the *hypochlorite of calcium*, the so-called *chloride of lime* or *bleaching powder*. This substance is prepared on a large scale by exposing slaked lime to the action of chlorine gas, whereby a solid mixture of hypochlorite and chloride of calcium is produced. It is soluble in water, and the solution is used for steeping the goods to be bleached. By itself it exerts no bleaching action whatever; but by exposing the fabrics wetted with it to the action of the carbonic acid in the air, or more quickly by steeping them in a bath of dilute sulphuric or hydrochloric acid, the salt is decomposed, and the liberated hypochlorous acid exerts its bleaching action on the tissues.

The strength of the chlorine-liquor is a matter of great importance. The stronger the liquor, the more rapid will be its action; but on the other hand, the greater will be the chance of injury to the goods. In practice it is not found safe to use a solution marking more than 2° or 3° of Baumé's hydrometer, or 0·5° of Twaddell's, equivalent to specific gravity 1002·5; and even this must be carefully removed by subsequent washing, and in some cases by the use of hyposulphite of sodium or other antichlors. (See ANTICHLOR.)

Wool and silk are for the most part bleached with sulphurous acid, chlorine and the hypochlorites being found to exert an injurious action upon them.

The rationale of bleaching is not thoroughly understood, but the most probable explanation of the action is, that it is due in all cases to oxygen in the peculiar active form called ozone. That active oxygen does possess this bleaching power is well-known: witness the action of peroxide of hydrogen on vegetable colours. Now in the old method of bleaching by exposure, light is an essential element of the action, the bleaching taking place much more quickly in sunshine than under a clouded sky. But Schönbein's investigations have also shown that ordinary atmospheric oxygen passes into the active state under the influence of light and moisture. Chlorine abstracts hydrogen from the colouring matter, and the oxygen thus set free produces the bleaching action. The action of sulphurous acid appears at first sight to be apposite to this, viz. deoxidising; but it is known from Schönbein's investigations, that an aqueous solution of sulphurous acid or an alkaline sulphite exposed to air and light quickly brings a portion of the oxygen in contact with it into the active state; hence also the bleaching action may in this case be due to oxidation. Sometimes, however, the sulphurous acid appears to unite directly with the colouring matter of the tissue to form a colourless compound.

The actual process of bleaching by means of chlorine or sulphurous acid is always preceded or accompanied by certain cleansing operations, consisting in washing with water, and boiling with alkaline leys or soap, the object of which is to remove resinous, fatty, and other impurities, either natural to the fibre or introduced accidentally or intentionally in the course of manufacture. All these substances impair the whiteness of the fabric, and often interfere greatly with the processes of dyeing and printing. Indeed, their removal by the means above mentioned, constitutes a very important part of the bleaching process, a large portion of the colouring matter being got rid of at the same time, so that the chlorine or sulphurous acid serves to give only the last finish. Cotton and linen goods are cleansed by washing with water and boiling with alkaline leys: formerly potash and soda were used for the purpose, but they are now nearly superseded by lime, at least for the first cleansing, as this substance, besides being much cheaper than the alkalis, is less likely to injure the fabric. Silk and wool are cleansed by scouring or boiling with water and soap, as they cannot bear the action of pure alkaline solutions.

Bleaching of Cotton. — The series of operations in the bleaching of cotton, may be thus generally described:

1. Boiling, or as it is technically called *bucking* or *bowking*, with milk of lime (1lb. of lime to 14 lbs. of cloth, and about as much water as will cover the cloth). This operation converts the resinous and fatty matters into lime-soaps.

2. Washing with water, in the dash-wheel, or other suitable machine, to remove the excess of lime and various soluble and mechanical impurities introduced in the process of manufacture.

3. *Souring* in hydrochloric acid of specific gravity 1·010 or 2° Twaddle, to decompose the lime-soaps and remove the lime. Dilute sulphuric acid is sometimes used, but hydrochloric acid is preferable, as chloride of calcium is much more soluble than the sulphate.

4. Washing again to remove excess of acid.

5. Bowking with a solution of soda-ash and resin (170 lbs. soda-ash, and 30 lbs. resin, to 3500 lbs. of cloth, and about the same quantity of water as in the lime-process). An imperfect soap is thus produced, which removes the rest of the fatty matter and dirt.

6. Washing, and then immersing the cloth in the chlorine-bath; this is called *chlorinating* or *chemicking*. The solution, which should be quite clear, has a specific gravity of 1002·5 or ½° Twaddle.

7. Souring in hydrochloric or sulphuric acid of 2° Twaddle, to set free the hypochlorous acid; then washing and drying.

The strength of the various liquors must be regulated according to the quality of the goods to be bleached, and the manner in which the operations are conducted: the preceding proportions of lime, soda, resin, &c. are given merely as examples. Sometimes carbonate of soda is used in the cleansing operations, sometimes a mixture of soda-ash and quick lime, which of course produces caustic soda. It is often found advantageous to perform the souring and chlorinating in two successive operations, the goods being washed between the two. This treatment is found to be less likely to injure the fibre than long-continued exposure to the action of the liquid in one operation. In all the operations, it is important to keep the cloth completely immersed in the liquid, and never to leave it exposed to the air before washing; because the acid or alkaline liquids, if allowed to become concentrated on it by drying, are sure to destroy the fibre.

Bleaching of Linen. — Linen contains a much larger quantity of colouring matter than cotton, and in bleaching loses nearly a third of its weight, whereas cotton loses only one-twentieth. This large amount of colouring matter is not natural to the flax, but is chiefly produced in the operation of steeping or *water-retting*, by which the textile fibres surrounding the stem of the plant are separated from the woody portion.

The colouring matter of steeped flax is insoluble in water, acids, and alkalis, but becomes soluble in alkalis after exposure to light or to the action of chlorine. Generally speaking, it is not found advantageous to rely on the action of chlorine alone for the bleaching of linen; the old method of exposure on the grass,—*crofting*, as it is called,—being almost always resorted to in addition. Moreover, it is not found possible to get rid of the colour entirely in one series of operations, several alternate exposures to oxygen or chlorine and to alkali being required to render the material perfectly white.

The following is an outline of the Irish method, as practised in the neighbourhood of Belfast:

1. *Steeping.*—After the linen has been scoured in the fulling-mill, warm water is poured upon it, and it is left immersed for two or three days, till acid fermentation sets in.—2. Boiling with potash-ley, soda-ley, or lime-water.—3. Washing.—4. *Crofting* or exposure on the grass for two or three days.—2′, 3′, 4′. The bowking, washing and crofting are repeated several times, six repetitions sufficing for the finer linens, and as many as twelve being sometimes required for the coarser.—5. *Souring* with hydrochloric- or sulphuric-acid of 2° Twaddle.—6. Washing, as in 3.—7. Soaping, that is, rubbing with solid soap or with very strong soap-suds.—8. Boiling in alkaline-ley of about ½ per cent.—9. Washing, as in 3 and 6.—10. Crofting for two days.—11. Chlorinating with a solution of hypochlorite of potassium, prepared by treating common bleaching powder with carbonate of potash. The liquor used is very weak.—12. Washing, as in 3 and 6.—13. Souring, as in 5, but with somewhat weaker acid.—14. Washing.—15. Soaping, as in 7.—16. Scalding, by immersing the cloth in soap-suds mixed with a little potash-ley of ½° B., and heating the liquid to boiling.—17. Washing.—18. Crofting.—19. Washing and drying.

Bleaching of Silk.—Raw silk contains, besides the true fibre, about 40 per cent. of foreign matter, viz. albumin, gelatinous substances, wax, fat, resin, and colouring matter. These substances are removed by boiling the silk in a strong solution of soap, then washing and rinsing. The silk after this treatment, is nearly white, but to render it quite white, it is sulphured, that is to say, suspended in the moist state in a large box in which sulphur is burned. About 1 lb. of sulphur is required for 20 lbs. of silk, and to obtain perfect whiteness, about four sulphurings, of twelve to sixteen hours each, are required.

As the silk loses considerably in weight, when cleansed in the manner above described, it is sometimes thought better to subject raw silk to the bleaching process without previous cleansing. For this purpose, a bath is used composed of 7 pts. hydrochloric acid and 3 pts. nitric acid, sometimes with addition of sulphuric acid, the liquid being diluted with water to 3° Bm. In this mixture, the skeins of silk are suspended, and repeatedly moved about for two or three hours, then wrung, twice washed, and afterwards sulphured. Sometimes the bleaching in the acid mixture is preceded by softening in a soap-bath; sometimes this softening process is made to intervene between the acid bath and the sulphuring.

Bleaching of Wool.—Wool is never bleached in the fleece, because its whiteness would be destroyed in the subsequent operations of spinning and weaving; the bleaching is, therefore, always performed on the yarn or on the woven fabric. A considerable portion of the dirt which adheres to the wool while on the animal, is removed by the washing which precedes shearing; this washing also removes the sweat, which is a kind of soap, chiefly composed of fatty matter and potash. But there still remains a quantity of free fat, which is generally removed by steeping and agitating it for ten or fifteen minutes in soap and water, or soda-ley, sometimes in putrid urine diluted with two or three measures of water, sometimes even in pure water. To prepare the wool for spinning, it is then greased with oil, as, without this preparation, it would be too harsh and very liable to tear. The grease thus added must of course be removed in the subsequent bleaching process. The treatment consists in passing the wool through a soda-bath, then through a soap-bath, washing in lukewarm water, and suspension in the sulphur chamber, this series of operations being repeated several times, and finally passing the bleached wool through a blue-bath, which is a very weak solution of soap containing hydrate of alumina and indigo. The sulphuring is sometimes omitted, and the cleansing is effected entirely by ammonia.

Bleaching of materials for Paper.—The rags used for making paper are bleached in the same manner as cotton goods. After being properly sorted and chopped or torn in pieces, they are bowked with lime-water, soured, washed in the rag-engine, which is a combined washing machine and filter, then chlorinated, soured, and washed again, and finally treated with a solution of hyposulphite of sodium to remove the last traces of chlorine. (See ANTICHLOR.)

"For bleaching old paper: Boil the printed paper for an instant in a solution of caustic soda. Steep it in soap-suds, and then wash it; after which it may be reduced to pulp. The soap may be omitted without much inconvenience.—For old written paper to be worked up again: Steep it in water acidulated with sulphuric acid, and then wash it well before it is taken to the mill. If the water be heated, it will be more effectual.—To bleach printed paper without destroying its texture: Steep the leaves in a caustic solution of soda, either hot or cold, and then in a solution of soap. Arrange them alternately between cloths, as paper-makers do thin sheets of paper when delivered from the form, and subject them to the press. If one operation do not render them sufficiently white, it may be repeated as often as necessary.—To bleach old written paper without destroying its texture: Steep the paper in water acidulated with sulphuric acid, either hot or cold, and then in a solution of oxygenated muriatic acid; after which immerse it in water, so that some of the acid may remain behind. The paper, when pressed and dried, is fit for use." *Ure.*

The *bleaching of straw* is effected by steeping it in hot water, heating it repeatedly during several days, and immersing it in weak solution of chloride of lime or of soda, alternately with weak alkaline leys.

Bleaching of Horse-hair.—White horse-hair requires further bleaching to adapt it to many purposes. The process consists in washing it in soda-solutions, not too strong, and at the heat of the hand, then hanging it up in the sulphur-chamber, and repeating these processes several times.

[For further details, see *Ure's Dictionary of Arts, Manufactures, and Mines,* i. 318, also *Muspratt's Chemistry,* i. 299.]

BLEACHING POWDER. *Chloride of Lime, Oxymuriate of Lime.* See HYPOCHLORITES, under CHLORINE.

BLEINIERITE. Basic Antimonate of Lead (p. 326).

BLENDE. Native SULPHIDE OF ZINC. (See ZINC.)

BLÖDITE. Probably the same as ASTRACANITE (i. 429).

BLOOD. The blood of the higher animals forms a rather viscous opaque liquid, heavier than water, and of more or less intense red colour, arterial blood being always lighter than venous. It is transparent in very thin strata. The specific gravity of normal human blood averages about 1·055, but under certain circumstances varies between 1·045 and 1·075; it is slightly less in women than in men, and still less in children. The specific gravity of arterial blood is rather less than that of venous. The blood of most domestic animals differs but little in specific gravity from that of man (specific gravity of bullock's blood = 1·060; of sheep's = between 1·050 and 1·058). The blood has always an alkaline reaction. When warm it has a peculiar odour, generally more powerful in the male than in the female.

From two to five minutes after the blood has left the circulation, it begins to *coagulate,* a film gradually extending from the surface and circumference, so that the whole becomes gelatinous in the course of from seven to fourteen minutes. The *coagulum* (*fibrin* and *blood-corpuscules*) then gradually contracts and separates from the watery portion of the blood (*serum*); and in from twelve to forty hours, the blood is completely resolved into serum and thick red clots, which swim beneath it. The blood of men coagulates more slowly, but yields a denser coagulum than that of women; in the embryo it coagulates imperfectly. Arterial blood coagulates more rapidly than venous. The presence of air and a rise of temperature promote coagulation; cold retards it.

The constituents of blood are partly in solution and partly suspended (blood-corpuscules). Swammerdam, in 1664, first observed corpuscules in the blood of the frog; he described them as oval. Leeuwenhoek (Phil. Trans. 1664, p. 23) found that human blood consisted of round bodies swimming in an opaline liquid, and that the colouring matter of the blood of mammalia, fish, and frogs was contained in these corpuscules, which were round in men, oxen, sheep, and rabbits, but oval in birds, frogs and fish. Later observers discovered that all blood-corpuscules are flattened. The coloured corpuscules consist of a colourless enevelope, the contents of which are red, or by transmitted light yellow, and each is slightly depressed and concave in the centre. In general they do not possess any nucleus, and only a few of them exhibit something approaching to one. The size of the red corpuscules varies considerably in different animals, the smallest being found in the blood of the *Moschus javanicus,* and having a diameter of 0·00208 mm. (Gulliver), and the largest in that of the *Cryptobronchus japonicus* (0·05623 mm. broad, and 0·0333 mm. long, V. d. Hoeven). The human corpuscules have a diameter of 0·00752 mm., those of the carnivora between $\frac{1}{[illegible]}$ and $\frac{1}{135}$ mm. and their thickness is generally $\frac{1}{4}$ or $\frac{1}{3}$ of their diameter. The blood-corpuscules of embryos are larger than those of the grown up animals of the same species. Milne-Edwards asserts that the size of the corpuscules is closely connected with the size of the organs of respiration. To prevent their shrinking up during measurement, C. Schmidt moistens a glass plate with an exceedingly thin layer of the blood to be examined, so that it dries up immediately. The corpuscules thus adhere by their flat sides to the glass, and remain of this same size when the serum has dried up. The blood of different animals may frequently be distinguished under the microscope by the size of the corpuscules.

According to Schmidt, the specific gravity of the blood-corpuscules of a healthy man varies between 1·0885 and 1·0889; in cholera it sometimes increases to 1·1025 or 1·1027. The red corpuscules *sink* in the serum; they are generally equally coloured; a few, however, are sometimes darker, sometimes lighter than normal corpuscules. The difference in colour is dependent upon the absolute amount of hæmatin in the corpuscules, the proportion of which relative to the serum influences the general colour of the blood. The form of the corpuscules also affects the colour of the blood, for if these be swollen by addition of water, they become more spherical, and the blood appears of a darker colour. Mulder supposes that the bright colour of arterial blood is due to the greater thickness of the enveloping membrane of the corpuscules. Nasse states that by the action of carbonic acid gas, the cells become darker in colour and turbid in the centre. All substances such as caustic alkalis, and several organic acids, which burst the corpuscules, or otherwise liberate their contents, turn the blood dark brownish-red, while those, such as nitrate and iodide of potassium, phosphate and carbonate of sodium, &c. which contract and so thicken the external membrane, render the blood of a lighter colour.

The average proportion by weight of moist blood corpuscules in a healthy man = 51·2 % (47·2—54·2 %). According to Vierordt, 1 cubic millimetre of blood contains 5,055,000 corpuscules. The amount of dry corpuscules in the blood of man is variously given = 12·9 % (Prévost and Dumas), 14·1 (13·1—15·2 %) (Becquerel and Rodier), 11·65 (Nasse). The blood of women contains fewer corpuscules than that of men, amounting to 36·924 % moist corpuscules (C. Schmidt), and 12·72 dry (11·3—13·75 %) (Becquerel and Rodier). The blood of middle-aged men and animals contains more corpuscules than that of older or younger individuals of the same species. The amount of corpuscules also varies in the blood of different animals, that of birds containing most, that of the carnivorous and herbivorous mammalia less, and that of cold-blooded animals by far the least, as will be seen from the following table, in which the *percentages* of dry corpuscules are given:

Chicken.	Pigeon.	Ox.	Sheep.
15·71 (Pr. and Du.)	15·57 (Pr. and Du.)	9·70 (Andral.)	9·35 (Pr. and Du.)
14·46 (Nasse.)		12·18 (Nasse.)	9·80 (Andral.)
15·00 (Poggiale.)	14·30 (Poggiale.)	12·30 (Poggiale.)	9·24 (Nasse.)
			10·20 (Poggiale.)

Dog.	Frog.	Eel.	Carp.
12·38 (Pr. and Du.)	6·90 (Pr. and Du.)	6·00 (Pr. and Du.)	8·23 (Berthold.)
12·38 (Nasse.)	4·58 (Berthold.)		
12·60 (Poggiale.)			

The proportion of corpuscules in the blood of different vessels also varies. In general, arterial blood contains fewer corpuscules than venous, the blood of the portal vein fewer than that of the jugular vein, while that of the hepatic vein contains far more than that of the portal vein, jugular veins, vena cava or splenic vein (Lehmann). Lehmann found 55·652 % moist corpuscules in the arterial blood of a horse, 48·996 in jugular blood, 55·688 in that of the vena cava.

Insufficient nourishment and long abstinence, as well as repeated blood-letting, diminish the quantity of blood-corpuscules; the amount increases if large quantities of fat are taken in the food. It is also influenced by disease, a constant increase being observed in plethora, in the earlier stages of heart-disease, in spinal irritation, and in cholera. Decrease occurs in all cases where the consumption of blood is greater than the supply, *e. g.* diarrhœa, intermittent fever, affections of the brain, and chlorosis (8·613 % Becquerel and Rodier). The percentage of water in the corpuscules bears a pretty constant relation to that of the serum, so that when the amount of water decreases in the serum, it also decreases in the corpuscules.

Colourless blood-corpuscules are always present in blood, but at least in the case of the warm-blooded animals, in much smaller quantity than the coloured corpuscules. They are generally almost spherical, but sometimes lenticular; they have a granulated envelope, and generally a round nucleus, which is more rarely oval or kidney-shaped, and strongly refracts light: sometimes it is formed of several small nuclei grouped together. They are identical with the lymph- and chyle-corpuscules, and do not differ much from the pus- and mucus-corpuscules. They are unelastic, and their envelope is so viscous that the corpuscules readily adhere to one another. They circulate less rapidly in the blood than the coloured corpuscules, and contain an albuminous liquid holding very minute granules in suspension. Dilute acetic acid gradually dissolves the external membrane. In human blood they measure 0·01128 mm. in diameter. They are specifically lighter than the red corpuscules, since they contain more fat and no hæmatin. In healthy blood they bear to the red corpuscules the ratio of 1 : 1·373 (Donders and Moleschott); the number increases during digestion and diminishes by fasting, the increase commencing thirty minutes after partaking of food, and lasting two hours. They increase in certain diseases, frequently in pneumonia and tuberculosis. In leuchæmia this increase often amounts to one-fourth of the blood-corpuscules. The splenic blood contains large quantities of colourless corpuscles, about one-fourth or one-third of the total amount of corpuscules.

Gases.—As early as 1674, free gases were supposed to be dissolved in blood, and the question was finally set at rest by the experiments of Magnus. The objection raised by Lagrange to Lavoisier's theory, that if combustion took place only in the lungs, the other parts of the body would have a lower temperature, led him to suppose that the blood merely dissolved the inhaled oxygen, and afterwards distributed it throughout the system. Fourcroy was, however, of opinion that combustion took place principally in the lungs, and that only a part of the oxygen was dissolved by the blood. H. Davy remarked that blood in contact with oxygen absorbs a certain quantity of the gas, giving off carbonic acid in exchange, and Nasse observed that blood in an atmosphere of hydrogen evolved carbonic acid. It has also been remarked that in an atmosphere of nitrogen, arterial blood evolves oxygen, but not venous blood. Mayow, Vogel, and others, obtained carbonic acid from the blood by means of the air-pump. Magnus also used the air-pump in his experiments, but collected the gas under mercury, and found the gases in *arterial* blood to consist of 14·5% N, 62·3% CO^2, and 23·2% O, in *venous*, 13·1% N, 71·6% CO^2, and 15·3% O. L. Meyer undertook a series of experiments on the gases of blood, under the guidance of Bunsen. The blood was diluted with ten times its bulk of water, and the gases were collected by boiling the liquid in vacuo at a very gentle heat: the free gases were thus obtained. A few crystals of tartaric acid were then added, and the blood again boiled, whereby the combined gas was liberated. The following table contains the quantities of gases (at 0° and 0·760m.) in 100 vols. of blood.

	Free Gas.	O.	N.	Free CO^2.	Combined CO^2.	Total. CO^2.	Total Gas.
Art. Carot. (Dog) (1)	20·88	12·43	2·83	5·62	28·61	34·23	49·49
„ „ „ (2)	25·50	14·29	5·04	6·17	28·58	34·75	54·08

Blood at 0° and 1 met. absorbs 1·151 vol. carbonic acid, besides 0·481, independently of the pressure (combined CO^2). Defibrinated calf's blood, free from air, absorbs under different pressures the same amount of oxygen (9·3% vol. at 0° and 0·760 m.) Serum absorbs a much smaller proportion of gases than defibrinated blood. The red colouring matter absorbs a considerable quantity of oxygen, and evolves a *little* carbonic acid. G. Harley found that blood, or defibrinated blood, absorbed oxygen when shaken up with air, and evolved carbonic acid, but in less quantity than corresponded to the oxygen absorbed.

It is difficult to explain satisfactorily why blood should absorb so much more carbonic acid than pure water at the same temperature; it is perhaps partly owing to the neutral alkaline carbonate in blood forming acid carbonate, but this does not account for all the carbonic acid absorbed. Liebig has remarked that water containing 1% phosphate of sodium absorbs twice as much carbonic acid as pure water, while water containing 15% chloride of sodium only takes up half as much. It is also supposed that oxygen, of which blood absorbs from 10 to 13% of its vol., and water only 0·925%, combines in a loose way with blood, like nitric oxide with ferrous sulphate, since the vol. of gas absorbed does not increase proportionally with the pressure (Liebig). It has also been shown that part of the oxygen thus taken up by blood cannot again be separated. (See GASES, ABSORPTION OF.)

Constituents of the coloured blood-corpuscules.—Berzelius has shown that the coloured corpuscules contain an albuminous substance (*globulin*) differing from albumin. Schmidt separated the corpuscules by means of sulphate of sodium, and found them to contain 87·59 globulin and 12·31% hæmatin. Mulder considers the outer membrane of the corpuscules to be binoxide of protein, a hypothetical substance; others have taken it for fibrin. Its composition does not appear to be fixed, since the membrane of different corpuscules is variously affected by the same reagents.

Blood-crystals; Hæmatocrystallin.—O. Funke first completely investigated the nature of the crystalline substance of the red corpuscles. Funke and Kunde obtain the crystals by adding to a drop of blood, water, ether, alcohol, or chloroform, allowing the mixture to dry slightly on a glass plate, and then covering the whole with a glass cover. Lehmann passes a slow stream of oxygen or nitrous oxide for about fifteen minutes into a mixture of blood and water, and afterwards carbonic acid, till the liquid turns bright red and becomes turbid, whereupon it crystallises. When a considerable quantity of blood is to be operated upon, it is best to leave it to coagulate, press the clot to remove the serum, cut it in pieces, and wash it on a linen filter with water till the filtered liquid amounts to about 1½ times or twice the volume of the water used. The liquid is then to be poured into a glass cylinder, oxygen gas passed into it for about half an hour, and then carbonic acid for ten or fifteen minutes, after which it is left at rest. If no crystals form after about two hours, the liquid must be mixed with ¼ of its volume of alcohol (Lehmann.) Light promotes the crystallisation, which is not caused by evaporation of water, since blood will crystallise as readily with twice its volume of water as with only half that quantity. It cannot be doubted that both oxygen and carbonic acid, by their chemical action on the contents of the corpuscules, are instrumental in the formation of the crystals. The form of the crystals varies in the blood of different animals; those obtained from the blood of men, most mammalia, and fish, form prisms; from the rat, mouse, and guinea-pig, tetrahedrons; from the squirrel, hexagonal tablets; and from the German marmot, rhombohedrons (of about 120°), or very thin hexagonal plates.* The tetrahedral crystals dissolve with peach-blossom-colour in 600 pts. of water, the prismatic with dark-red colour in 94 pts. water. Nitric acid turns the crystals almost black, but dissolves them on warming, and acquires a yellow colour. Their solution is decolorised by chlorine, which precipitates white flakes; it is turned dark brownish-red by carbonic oxide, and rendered turbid and brownish-red by nitrogen. The same sized crystals from the same blood often differ in intensity of colour and have probably not always the same composition. They seem to be an albuminous substance.

The solution of the tetrahedral crystals coagulates at about 63° C., that of the prismatic crystals between 64° and 65°. The crystals exhibit, according to Lehmann's analysis, the percentage composition of the albuminoïds:

Carbon	55·41	55·24	55·18
Hydrogen	7·08	7·12	7·14
Nitrogen	17·27	17·31	16·40
Sulphur	0·25	0·21	0·25
Oxygen	19·99	25·12	20·03
	100·00	100·00	100·00

Hæmatin is peculiar to the blood-corpuscules of vertebrate animals, and in some way combined with the remaining albuminous contents of the corpuscules. It is obtained as an amorphous blackish-brown substance, by treating the corpuscules with sulphate of sodium, extracting the residue with alcohol containing sulphuric acid, and treating with ammonia, water, alcohol, and ether. It is insoluble in water, alcohol, ether, acetic ether, and oils, both fat and volatile, but readily soluble in alcohol containing sulphuric or hydrochloric acid. It is not dissolved by concentrated mineral acids. Aqueous or alcoholic solutions of alkalis or their carbonates dissolve hæmatin in all proportions. A sulphuric acid solution of hæmatin which has been turned red by addition of alkali, exhibits dichroïsm, appearing green by transmitted and red by reflected light. If hæmatin be allowed to stand in contact with pure concentrated sulphuric acid, it may be obtained perfectly free from iron, without suffering any perceptible change in its properties. Berzelius found in the dry blood corpuscules of men and oxen 0·38 % metallic iron, and since Mulder has found 6·64 % iron in hæmatin, the corpuscules would contain 5·72 % hæmatin, and the blood 0·732 %. Becquerel and Rodier found in blood, 0·0565 % iron, and 14·11 % corpuscules, which would give 6·02 pts. hæmatin to every 100 pts. corpuscules. In disease, the proportion of hæmatin to the whole blood probably varies with the corpuscules. It is not known whether there is a fixed relation between hæmatin and the albuminoïd of the corpuscules. Mulder assigns to it the formula $C^{44}H^{22}N^{3}O^{6}$. The arterial blood of the horse contains rather less hæmatin than that of the outer jugular vein; the corpuscules of the liver-blood contain far less than those of the *vena porta*. The proportion of iron to dry corpuscules in arterial blood = 1 : 394; in that of the jugular vein 1 : 390; of the vena porta 1 : 312; of the liver 1 : 500 (Lehmann.) Poggiale found 0·126 % ferric oxide in human blood, in that of the ox 0·125, calf 0·111, dog 0·145, sheep 0·106, chicken 0·075.

A substance called *hæmatoïdin* has been observed in blood extravasated in the tissues of living animals. It is sometimes amorphous, in grains and little globules; sometimes in crystals belonging to the monoclinic system. It is transparent, strongly refracting, yellowish-red or ruby-red, insoluble in water, alcohol, ether, acetic acid, and dilute mineral acids. It generally turns ardent red on addition of potash, gradually disintegrates, and splits up into red granules, which gradually dissolve. The hæmatoïdin is not reprecipitated by neutralising the alkali. By the action of concentrated sulphuric acid, the sharp contour of the crystals vanishes, and the colour of the round concretions first turns brownish-red, then green, blue, and rose, and finally dirty yellow. In the liquid, iron may sometimes be detected, but not always. According to Robin, its formula is $C^{14}H^{18}N^{2}O^{3}$.

The nature of the *nuclei* which sometimes occur in the corpuscules is unknown.

A considerable quantity of the *fat* of blood occurs in the corpuscules, nearly the whole of the so-called phosphorised fats being contained therein. Lehmann found 2·214 and 2·284% fat in the dry corpuscules from bullock's blood. The ethereal

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* Figures of these crystals are given in Funke's Atlas of Physiological Chemistry (Leipzig, 1853, also published by the Cavendish Society); and in the Handwörterbuch der Chemie, 2te Aufl. ii. [2] 136.

extract of these corpuscules yielded 22 % acid ash, consisting of acid phosphate of sodium, from which it is probable that phosphoglyceric acid is contained in the corpuscules. The corpuscules in the blood of different vessels do not contain the same amount of fat. In the moist corpuscules of the carotid artery of the horse, were found 0·608 % fat; in the external jugular vein 0·652 %; in the vena porta 0·752; in liver-blood 0·684. Dry corpuscules separated from arterial blood by sulphate of sodium contained 1·842 % fat; from venous blood 3·595 %.

The solid constituents of the corpuscules contain rather less than 6 % *extractive matter*, the nature of which is unknown. They also contain a free or loosely combined nitrogenised organic acid.

Moist corpuscules contain on the average 68·8 % *water* (Lehmann). Taking into account the amount of serum enclosed in the coagulum, the corpuscules contain a much smaller proportion of soluble *salts* than the serum. It will be seen from the analyses by Schmidt (p. 611), which are the most trustworthy, that the corpuscules contain principally phosphates and potassium salts, and, in smaller quantity, chlorine, sulphuric acid, soda, and earths, while the serum contains proportionally less chloride of potassium and phosphate of sodium, and more chloride of sodium, sulphuric acid and earths. In man the moist corpuscules contain 0·7282 % salts. The blood of those animals which contained most corpuscules also contains most alkaline phosphates (Nasse). The corpuscules contain less earthy phosphates than the serum. Iron belongs almost exclusively to the red corpuscules (hæmatin). Clear serum contains no iron. (Nasse and Schmidt).

Fibrin. — As already stated, the spontaneous coagulation of the blood is caused by the separation of the fibrin, which at the same time encloses all the corpuscules and a portion of the serum. As soon as the blood has left the body, a film gathers on the surface of the liquid, extending in the form of a star, from the sides of the vessel towards the centre; a clot, adhering to the sides of the vessel, then forms. Often, within two minutes after the blood has been collected, it becomes viscid and gelatinous, and after a time a few drops of liquid, gradually increasing in quantity, separate from the jelly, till the coagulum swims in the serum. According to circumstances the coagulum is more or less contracted, consistent, viscous, and elastic. If the coagulation be observed under the microscope, exceedingly fine straight threads will be seen to shoot out from various points between the corpuscules, and, gradually increasing in length, to cross one another, so that finally the whole forms a network enclosing the corpuscules. If the amount of fibrin is small in comparison to the corpuscules, the coagulum is comparatively light; denser, on the contrary, when the amount of fibrin is large. A large quantity of water diminishes the consistence of the coagulum. Various salts have the property of retarding or entirely preventing the coagulation of blood. The alkalis and their carbonates and acetates have this effect, and rather strong solutions of nitrate of potassium, nitrate of calcium, and chloride of ammonium in a less degree. Most dilute acids also maintain the fluidity of blood, though they render it rather more viscous. The venous blood of a healthy man contains between 0·203 and 0·263 % fibrin (Scherer), 0·220 (average, Becquerel and Rodier), 0·250 % (Denis). Arterial blood contains more fibrin than venous. (See Fibrin.)

Constituents of the Serum.—The average specific gravity of serum = 1·028; it is less variable than the specific gravity of blood. The amount of *water* in the serum varies between 88 and 95·6 %, averaging 90·5 or 90·6 % (Nasse). Women's blood contains more water than that of men. According to C. Schmidt, the serum of man contains 90·884 % water, and that of woman 91·715; and, according to Nasse, the serum of pregnant women is more aqueous than of others. At an advanced age, the amount of water increases considerably. The following table contains the percentages of water in the serum of different animals:—

Ox.	Sheep.	Dog.	Chicken.
90·8 (Nasse.)	91·5 (Du. and Pr.)	92·6 (Du. and Pr.)	92·5 (Du. and Pr.)
91·6 (Berthold.)	91·8 (Nasse.)	91·2 (Nasse.)	93·1 (Nasse.)

Pigeon.	Frog.	Eel.
94·5 (Du. and Pr.)	95·0 (Du. and Pr.)	90·0 (Du. and Pr.)

According to most observations, the serum of arterial blood contains more water than that of venous blood. Simon found in the arterial blood of two horses, 2·734 % more water than in the venous blood, and, according to Nasse, arterial blood contains 5·0 % more water than venous. As a general rule, the amounts of water in the serum and of corpuscules in the blood are inversely proportional. An absolute diminution of water has only been remarked in cholera.

Albumin is the most abundant of the constituents of the serum, amounting to between 6·3 and 7·1 % of normal blood, and between 7·9 and 9·8 % of normal serum. Neutral albuminate of sodium, which becomes turbid on addition of water, occurs not only in morbid blood, but also in the blood of the spleen. The serum of the blood of the vena porta gives less turbidity, and that of the liver-blood more, than of the spleen. When the alkaline serum of liver-blood is neutralised with acetic acid, the albumin does not coagulate on boiling till after several hours, while that of the vena porta and other veins, as well as of the arteries, speedily coagulates on addition of acetic acid and boiling. Hoppe is of opinion that the albumin in serum is not dissolved, but merely suspended in a state of fine division. According to Becquerel and Rodier, normal man's blood contains 6·94 % (6·2—7·3 %) albumin, and that of women 7·05 (6·5—7·55) %. The blood of pregnant women was found to contain from the 2nd to the 7th month, 7·0—6·8 % albumin, and in the last two months, 6·8—6·4 %. (J. Regnault). Arterial blood contains less albumin than venous, and the amount in liver-blood increases considerably during digestion; it decreases in scurvy, puerperal fever, and Bright's disease, and increases in intermittent fever, cholera, &c. In typhus, it amounted to 6·5 %, and in Bright's disease to only 4·93 %.

Fats.—But few free fats are found in serum; they occur chiefly saponified. Chevreul and Babington first discovered the presence of normal fats in blood. Oleic, margaric, and stearic acids, both free and saponified, have been detected in the serum of bullock's blood, and cholesterin is constantly present. Boudet describes, as a fat peculiar to the serum, a substance extracted from its residue by hot alcohol (serolin), which Gobley considers as a mixture of oleïn, margarin, cholesterin, and cerebrin. According to Chevreul, phospholeïc acid (cerebrin) is contained in the fibrin and serum. Compared with the corpuscules, that of the serum is more crystalline, less viscous, and colourless. Normal serum contains 0·2 % fat, and its solid residue 2·22 % (Simon, Nasse, Becquerel). The amount of fat in the blood is not increased by food rich in fat, nor is it diminished by nourishment free from fat. During digestion, the amount of fat in chyle and in the blood of the vena porta, has been found to increase considerably, so as occasionally to render the serum turbid. According to Becquerel and Rodier, the blood of women contains 0·57 p. m. fat and soaps, and that of men 0·69 p. m. Serum of arterial blood contains less fat than that of venous, and the vena porta blood is richer than the jugular. Becquerel and Rodier have found that, almost at the commencement of every acute disease, the proportion of fat (especially cholesterin), in blood increases, as well as in some chronic diseases, particularly in liver diseases, Bright's disease, tuberculosis, and cholera.

Little is known of the *extractive matter* of the serum; it varies between 0·25 and 0·42 %. Lehmann found more in the arterial than in the venous matter of the horse.

Sugar (grape-sugar), is a normal constituent of blood. The blood of the vena porta contains but traces, while that of the liver contains larger quantities. In normal bullock's blood, it varies between 0·00069 and 0·00074 % (Lehmann). The blood of a dog contained 0·0015, and of a cat 0·0021 %. In the blood of diabetic patients Lehmann never detected more than 0·047 % sugar. The amount varies with the nature of the food. *Urea* occurs in healthy blood to the amount of 0·0142—0·0177 %. It has been detected by evaporating large quantities of serum and adding nitric or oxalic acid to the residue. The quantity increases considerably in Bright's disease (1·5 % in serum, Bright and Babington), and in cholera (0·14 %). *Uric acid* has been found in the blood of healthy as well as of diseased persons. Garrod found between 0·0012 and 0·0055 in the serum in a case of Bright's disease. *Creatine, creatinine, hippuric acid*, and *hypoxanthine*, have also been detected. According to Musing, *alcohol* has been detected in the blood of men who had died from drinking brandy. Matteucci states that goat's blood warmed with sulphuric acid evolves *caproic acid*. Scherer has detected *lactic acid* in a case of puerperal fever. Fourcroy and Vauquelin and others state that they have found bile-constituents in healthy blood; they sometimes occur in morbid blood. *Leucine* and *tyrosine* occur in small quantities in liver and portal blood, in diseases of the liver. Little is known of the *colouring matters* proper to the serum. An intense yellow coloration of the serum is often due either to bile-pigment, which may be detected not only in icterus, but also in pneumonia. Black, scarcely yellow, brown, or red granules of pigment are said to have been detected in the heart, large vessels, liver, and spleen, after intermittent fever. Blood contains *neutral carbonate of sodium* (0·1628 % in bullock's blood, Lehmann), probably as acid carbonate (Lehmann, Liebig). Meyer concludes from his experiments that it is not present as acid carbonate. Blood seldom contains *sulphates*, and never more than traces; it contains *silicic acid* (Millon), and according to G. Wilson, traces of *fluorine*. Normal blood never contains *ammonia*, but that alkali is sometimes found in disease (cholera, &c.)

Salts.—The serum of man's blood contains 0·88 % (av.) salts, that of women 0·81 %. Lehmann gives the following composition of the ash according to the best analyses: 61·087 % chloride of sodium. 4·085 chloride of potassium, 28·880 carbonate of sodium, 3·195 phosphate of sodium (Na^2HPO^4), 2·784 sulphate of potassium. The serum of grown-up animals contains more salts than that of the young; the serum of the calf, however, contains 1·12 % salts, while that of the cow contains 0·99, and of the ox 0·87 % (Nasse and Poggiale). The blood of cats, goats, and sheep, contains the most salts; of birds, men, and pigs, less; and of dogs and rabbits the least. Arterial blood serum is somewhat richer in salts than venous, and the serum of portal blood contains considerably more than that of the jugular vein. The kind of nourishment has great influence on the amount of salts, and of their several constituents. Plouviez and Poggiale found that in the blood of animals to whose food common salt had been added for several months, the percentage of salt rose from 0·44 to 0·64, an increase due chiefly to chloride of sodium. The amount of salts is also greatly influenced by disease, being particularly small in violent inflammations, and increasing in typhus, &c. Weber found 1·19 % *silica* in the ash of bullock's blood.

The amount of salts, exclusive of iron, in man's blood = 0·728 %, woman 0·896, dog 0·713 %. Some chemists think they have detected *manganese* in blood, but its presence is doubtful. Millon found *copper* in the blood of soldiers whose food had been prepared in copper vessels, and others have detected traces in the blood of men and beasts. It is said always to occur in the ash of the blood of *Limulus Cyclops*. Millon also detected *lead* in blood.

ANALYSIS OF BLOOD.—The amount of *water* in blood is easily estimated by evaporating a weighed quantity, and drying the residue at 120°—130° C.

To determine the *fibrin*, the blood, as it runs from a vein, is received in a tared vessel, and stirred for 5 to 10 minutes with a glass rod, the weight of which is included in the tare, till the fibrin is completely separated. The blood, together with the separated fibrin, is then weighed, strained through linen, and the fibrin which remains thereon is placed for some time in water, then dried, well boiled with alcohol and ether, to free it from fat, and weighed after drying at 120° C. (Becquerel and Rodier).—Another method of estimation is to leave a weighed quantity of blood to coagulate at rest, tie up the clot in a fine linen bag, after it has contracted as much as possible, knead it first by itself, afterwards with water, and treat the residue as above. (Scherer.)

Estimation of Albumin and other Matters coagulable by Heat.—A weighed quantity of the blood, slightly acidulated with acetic acid, is added by drops to boiling water, the liquid is poured through a weighed filter, and the coagulum collected thereon; it is then washed on the filter with boiling water, and dried, first at a gentle heat, afterwards at 120° to 130° C. The residue may be freed from fat by treatment with boiling ether. If the blood had not been previously freed from fibrin, the weight of that substance, determined as above, must be deducted from the total weight of the coagulum.

Estimation of the Extractive Matter.—The filtrate obtained in the last determination is evaporated on the water-bath in a tared platinum basin, the residue dried at 120° C., weighed, and burnt in a muffle at as low a heat as possible. The weight of the ash, deducted from that of the total dried residue, gives approximately the amount of extractive matter.

Estimation of Fat.—A quantity of blood (which need not be weighed) is dried at 100° C., the residue is pulverised and dried at 120°, and a weighed portion thereof is treated with ether in a flask: the ether is passed through a small filter into a tared platinum capsule; and the treatment of the residue with ether is repeated several times. The collected ethereal solution is carefully evaporated, and the residue dried at 100° C. As the weight of the solid constituents of the blood has been previously determined, the quantity of blood from which this amount of fat has been obtained may be calculated from that of the residue which was subjected to treatment with ether.

Estimation of Mineral Constituents.—A weighed quantity of the blood is dried, mixed with ignited carbonate of sodium, then dried and incinerated in the muffle at the lowest possible temperature. (See ASH OF ORGANIC BODIES, p. 418.)

Separate Estimation of the Serum and Coagulum, with their Constituents.—The fresh blood is collected in a tared cylindrical vessel, having a ground edge, and not too shallow; it is covered with a glass plate and left to stand till the coagulation is complete, after which the edge of the clot is detached from the side of the vessel by means of a needle. The blood is then weighed, and after the clot has contracted as much as possible, the serum is poured off, and the quantity of albumin, &c., contained in it is determined as above described. The clot and the inner surface of the vessel are then freed from serum as completely as possible by wiping with bibulous paper, and the clot is weighed on the vessel. This weight, deducted from the total weight of the blood, gives the proportion of serum.

The clot contains the blood-corpuscules, the fibrin, and a certain quantity of serum; the amount of water contained in it may be determined by drying at 120° to 130° C., but there is no known method of directly estimating the amount of the blood-corpuscules. Prevost and Dumas estimated it approximately on the assumption that the water contained in the clot is all due to adhering serum, and accordingly deducting from the weight of the dried clot an amount of serum-constituents corresponding to the quantity of water in the clot, together with the amount of fibrin separately determined. As, however, the blood-corpuscules themselves contain water, this method necessarily makes the quantity of dry corpuscules too small.

According to C. Schmidt, the clot contains a quantity of serum amounting to $\frac{1}{8}$ of its volume, and the weight of the moist blood-cells is four times as great as that of the dry clot, as determined by the method of Prevost and Dumas. Hence, when the constituents of the serum and coagulum have been determined as above, and from the weight of the coagulum, a deduction is made of the quantity of serum-constituents corresponding to $\frac{1}{8}$ of the weight of the moist coagulum, the composition of the corpuscules may be calculated.

The separation of hæmatin from globulin cannot be effected; but if the quantity of iron in the dry coagulum be determined, the amount of blood-pigment may be calculated on the supposition that this pigment contains 6·64 per cent. of iron. (Strecker, Handw. d. Chem. ii. [2] 115).

1000 pts. Blood-corpuscles contain:

Water	688·00
Solid constituents	312·00
Density	1·0885
Hæmatin	16·75
Globulin and membrane of corpuscules	282·22
Fat	2·31
Extractive matter	2·60
Mineral matter (without iron)	8·12
Chlorine	1·686
Sulphuric acid	0·066
Phosphoric acid	1·134
Potassium	3·828
Sodium	1·052
Oxygen	0·667
Phosphate of calcium	0·114
Phosphate of magnesium	0·073

1000 pts. Serum contain:

Water	902·90
Solid constituents	97·10
Density	1·028
Fibrin	4·05
Albumin	78·84
Fat	1·72
Extractive matter	3·94
Mineral matter	8·55
Chlorine	3·644
Sulphuric acid	0·115
Phosphoric acid	0·191
Potassium	3·323
Sodium	3·341
Oxygen	0·403
Phosphate of calcium	0·311
Phosphate of magnesium	0·222

Mean Composition of Male and Female Blood (Becquerel and Rodier).

	Male	Female.
Density of defibrinated blood	1060·00	1017·50
Density of serum	1028·00	1027·40
Water	779·00	791·10
Fibrin	2·20	2·20
Fatty matters	1·60	1·62
Serolin	0·02	0·02
Phosphorised fat	0·49	0·46
Cholesterin	0·09	0·09
Saponified fat	1·00	1·04
Albumin	69·40	70·50
Blood-corpuscules	141·10	127·20
Extractive matters and salts	6·80	7·40
Chloride of sodium	3·10	3·90
Other soluble salts	2·50	2·90
Earthy phosphates	0·33	0·35
Iron	0·57	0·54

1000 pts. Blood contain (Schmidt):

	Man.	Woman.	Dog.
Moist corpuscules	513·02	396·24	543·56
Serum	486·98	603·76	456·44

Salts in 1000 pts.:

	Corpuscles.	Serum.	Corpuscles.	Serum.	Corpuscles.	Serum
Sulphate of potassium	0·132	0.281	0·157	0·217	0·309	0·502
Chloride of potassium	3·679	0·359	3·414	0·447	0·557	0·118
Chloride of sodium	—	0·546	—	5·659	2·485	5·342
Phosphate of potassium	2·343	—	2·108	—	—	—
Phosphate of sodium	0·633	0·271	—	0·443	2·803	0·311
Potassa	—	—	0·857	—	—	—
Soda	0·341	4·532	2·205	1·074	0·861	1·726
Phosphate of calcium	0·094	0·298	0·218	0·550	0·110	0·841
Phosphate of magnesium	0·060	0·218				

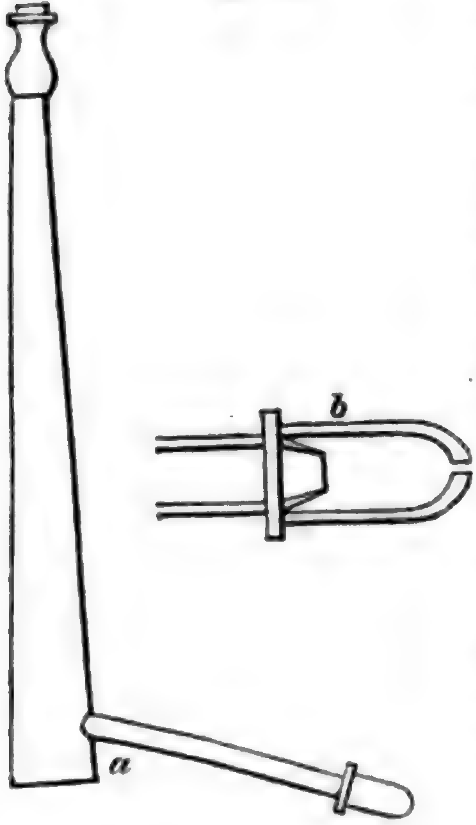
C. E. L.

BLOODSTONE. A variety of JASPER (*q. v.*)

BLOWPIPE. An instrument for directing a stream of air through a flame, either by blowing with the mouth or with bellows. The flame of a candle, of a lamp with a simple wick, or of an ordinary gas-jet, consists of three parts. The dark central portion immediately surrounding the wick or burner, consists of combustible gaseous matter, not yet burned; this is surrounded by a highly luminous cone, which deposits soot on a cool body held within it; and outside of all is a thin pale blue envelope which gives little light, but has a very high temperature. It is here that the combustion is most complete, the carbon and hydrogen finding sufficient oxygen to convert them into water and carbonic acid. But in the middle luminous cone, the supply of oxygen is not sufficient for complete combustion, and consequently the hydrogen, which burns most easily, takes up the whole or the greater part of it, while the carbon is set free in the form of minute solid particles. If now a jet of air be directed through the middle of the flame, a double combustion takes place, the combustible matter uniting on the outside with the oxygen of the air, and in the interior with that which is supplied by the blast. In this manner, an intensely hot flame is produced, applicable for fusions, reductions, and a variety of operations in chemical analysis; and likewise for soldering metals and working glass.

The best and cheapest form of the mouth-blowpipe for chemical purposes, is that invented by Black. It consists of a tube of tin-plate (*fig.* 101), about 7 inches long, and $\frac{3}{4}$ of an inch broad, tapering to $\frac{1}{4}$ of an inch, where a small mouth-piece is soldered. At the wide end *a* is inserted a small cylindrical tube of brass, about 2 in. long, supporting the nozzle, which may be of brass or platinum.

Fig. 101.

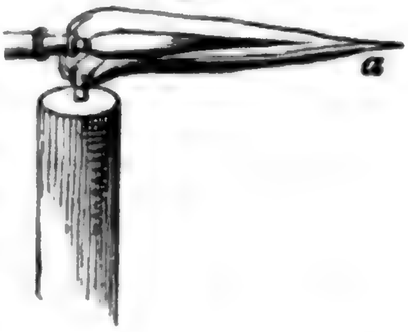


The tube is slightly conical at the end where the jet is fixed, and the latter is thus made to fit on without a screw, which would soon be injured by the high temperature to which it is exposed, and would then be difficult to remove for the purpose of cleaning. The nozzle is drilled from a solid piece of metal, and in the form shown at *b* in the figure. One of the chief excellencies of this form of blowpipe, is the efficient manner in which it condenses and retains the moisture of the breath, and prevents its projection on the heated assay. The blowpipe may also be provided with a moveable trumpet-shaped mouthpiece, against which the lips, partially open, may be pressed during the act of blowing; in this manner, a strong blast may be kept up for a considerable time with very little fatigue. The use of such a mouthpiece is strongly recommended by Plattner in his valuable treatise on the blowpipe; but it is scarcely necessary, excepting when the blast has to be kept up for a long time, as when the blowpipe is used for quantitative analysis.

To use the mouth-blowpipe with success, it is necessary to acquire the art of keeping up a steady blast of air for some time. For this end, the air must be supplied from the mouth, not directly from the lungs, which could not, without fatigue, afford a sufficient stream. The mouth-piece of the instrument being placed between the lips, the mouth is to be filled with air till the cheeks become distended as in playing on a wind instrument. The current of air is then forced through the tube by the action of the muscles of the cheeks, and during the blast, the communication between the chest and mouth is closed, respiration being carried on through the nostrils. The mode of effecting this is difficult to describe, but the right method of blowing is easily acquired by a little practice.

The quality and intensity of the flame vary considerably according to the strength and direction of the blast. If the nozzle of the blowpipe is inserted into the middle of the flame, a little above the wick, as shown in *fig.* 102, an elongated flame is produced, consisting of an outer and an inner cone, the former having a yellow, the latter a blue colour. The outer flame is an *oxidising* flame. An oxidable substance, such as lead or copper, placed at or just beyond the point *a* of this flame, is strongly heated in contact with the oxygen of the air, and is therefore brought just into the condition for taking up oxygen. The greatest heat is at the point of the inner flame, the combustible gases being there supplied with just the quantity of oxygen required to consume them; and between this and the point of the exterior flame, is a quantity of combustible manner, very hot, but not yet burned, and therefore disposed to take oxygen from any compound containing that element. This part of the flame is therefore a *reducing* flame. A piece of ordinary glass containing lead, turns black and opaque when heated in this part of the flame, in consequence of the reduction of the lead; but by afterwards heating it in the outer flame, the lead is reoxidised, and the transparency restored.

Fig. 102.



But the reducing power of a flame produced in the manner just described, is not very great, as any one may convince himself by trying to reduce oxide of copper or oxide of tin in it without the aid of a reducing agent. The flame is for the most part an oxidising flame, especially if the aperture of the blowpipe is large and gives a good supply of air. To obtain a good reducing flame, it is necessary to use a blowpipe with a small aperture, and to adjust the point, not within, but just outside the flame, and to blow rather over than through the middle of the flame. In this manner, the flame is less altered in its general characters than in the former case, the chief part consisting of a large and luminous cone, containing a considerable quantity of free carbon in a state of intense ignition, and just in the condition for taking up oxygen.

Substances to be heated in the blowpipe flame, are supported, sometimes on charcoal, sometimes in spoons or forceps made of platinum, or on platinum foil or wire, sometimes on small capsules made of clay or bone-earth. Charcoal is used chiefly in experiments of reduction. The substance to be heated is placed in a small hole scooped in the side of the charcoal, not at the ends, because in the latter position, it is more likely, when in the fused state, to sink into the pores of the charcoal. Clay basins are chiefly used in the quantitative assaying of ores. They are made of fire-clay kneaded into a stiff paste with water, pressed into shape in a box-wood mould (*fig.* 103), then dried and calcined. Instead of these, however, very thin porcelain basins, which may be procured ready made, may be used with advantage. Basins or cupels of bone-earth made in a similar manner, are used for cupelling silver and gold with lead. The oxide of lead formed in the process, sinks into the porous support leaving the silver or gold in the form of a metallic button.

Fig. 103.

Blowpipe Analysis.—The blowpipe is an indispensable instrument in qualitative analysis, as it serves to recognise the presence of many substances with greater facility and certainty than could be obtained by analysis with liquid reagents, especially when the quantity of substance to be operated on is but small. Generally speaking, however, it is not safe to trust to the indications of the blowpipe alone, inasmuch as many substances give but indistinct reactions when submitted to this mode of examination, and are apt to be completely overlooked when present together with others whose indications are more decided. In a mixture of iron, nickel, and cobalt, for example, it would be scarcely possible by the blowpipe alone to recognise anything but cobalt, even though that metal might be present in small proportion only as compared with the others. It is best, therefore, to use the blowpipe, and in general, the mode of analysis by the dry way, as a means of determining the general character of a compound or mixture, and detecting certain of its constituents, and thus obtaining an indication of the best mode of proceeding with the more complete analysis by the wet way.

A concise account of the behaviour of the several elementary bodies, and their principal inorganic compounds when heated *per se*, and with certain reagents, is given in the article Analysis (Inorganic), (p. 213); and these characters will be described in greater detail in treating of the several elements and compounds. The table on

Behaviour of Metallic Oxides before the Blow-

A clear bead is formed by fusing the flux on a loop made at the end of a platinum-wire: the bead is
in the reducing flame, it is sometimes advisable to employ charcoal instead of platinum-wire. The
employed. In this table h. signifies hot; c. cold; supers. that the bead is super-

Colour of the Bead.	With Microcosmic Salt.	
	In outer or oxidising Flame.	In inner or reducing Flame.
Colourless.	*Silica* swims undissolved. *Alumina, Stannic oxide.* All *Alkaline earths,* and *Earths* (supers. opaque). *Tantalic, Columbic, Titanic, Tungstic anhydrides; Zinc-, Cadmium-, Lead-, Bismuth-, Antimony-oxides* not sat.: (supers. yellowish).	*Silica* swims undissolved. *Alumina.* All *alkaline earths* and *earths* (supers. opaque). *Ceric, Didymic, Manganic, Stannic oxides.*
Yellow or brownish.	h. not sat. *Ferric* and *Ceric oxides.* h. *Vanadic anhydride, Uranic oxide, Oxide of Silver.* c. *Nickel-oxide.*	h. *Ferric oxide* (reddish), *Titanic anhyd.*
Red.	h. *Nickel-oxide.* h. supers. *Ferric* and *Ceric oxides.*	h. *Ferric oxide.* c. *Titanic* and *Tungstic anhydrides containing iron* (blood-red). *Cupric oxide.*
Violet or Amethyst.	*Manganic* and *Didymic oxides.*	c. *Titanic anhydride. Columbous anhydride* (not sat.).
Blue.	*Cobalt-oxide.* c. *Cupric oxide.*	*Cobalt-oxide. Tungstic anhydride. Niobous anhydride* (supers.)
Green.	h. *Cupric oxide, Molybdic anhydride, Ferric oxide containing cobalt or copper. Chromic* and *Uranic oxides.*	*Chromic* and *Uranic oxides, Vanadic* and *Molybdic anhydride.*
Grey and Opaque.		c. *Oxides of Silver, Zinc, Cadmium, Lead, Bismuth, Antimony: Tellurous anhydride.*

pipe with Microcosmic Salt and Borax.

dipped into the finely-powdered substance under examination, and again heated. In heating
colour of the bead frequently varies with its temperature, and with the quantity of oxide
saturated with oxide ; not sat. that it is not completely saturated with oxide.

With Borax.	
In outer or oxidising Flame.	In inner or reducing Flame.
Silica, Alumina, Stannic oxide.— Supers. opaque : *Alkaline earths* and *Earths, Oxide of silver, Tantalic, Columbic, Tellurous anhydrides.*— Not sat.: *Titanic, Tungstic, Molybdic anhydrides, Zinc-, Cadmium-, Lead-, Bismuth-, Antimony-oxides.*	*Silica, Alumina, Stannic oxide.*— Supers. opaque: *Alkaline earths* and *Earths, Lanthanic and Ceric oxides, Tantalic anhyd. Manganic* and *Didymic oxides.* h. *Cupric oxide.*
h. *Vanadic anhydride.* h. not sat. *Ferric* and *Uranic oxides.* h. supers. *Lead-, Bismuth-,* and *Antimonious oxides.*	*Tungstic anhydride; Titanic, Vanadic,* and *Molybdic anhydrides* (brownish).
h. *Ceric* and *Ferric oxides.* c. *Nickel-oxide* (red-brown). h. supers. *Chromic oxide.*	c. *Cupric Oxide* (supers. opaque).
Manganic and *Didymic oxides. Nickel-oxide containing cobalt.*	
Cobalt-oxide. c. *Cupric oxide.*	*Cobalt-oxide.*
c. *Chromic oxide, Vanadic anhyd.* h. *Cupric oxide, Ferric oxide containing copper or cobalt.*	*Ferric, Uranic, Chromic oxides.* c. *Vanadic anhydride.*
	The same as with microcosmic salt. Also *Nickel-oxide,* and (supers.) *Columbous anhydride.*

page 614 (taken from Conington's "Handbook of Analysis,") exhibits in a convenient form the colours imparted by metallic oxides to borax and microcosmic salt, when heated therewith in the oxidising and reducing flames. [For further details, see "Chemical Manipulation," by C. Greville Wliliams, London: Van Voorst; also, especially for the method of Quantitative Analysis with the blowpipe: Plattner's "Probierkunst mit dem Löthrohre," or the translation of that work "On the Use of the Blowpipe, &c.," by Dr. Muspratt, London, 1850.]

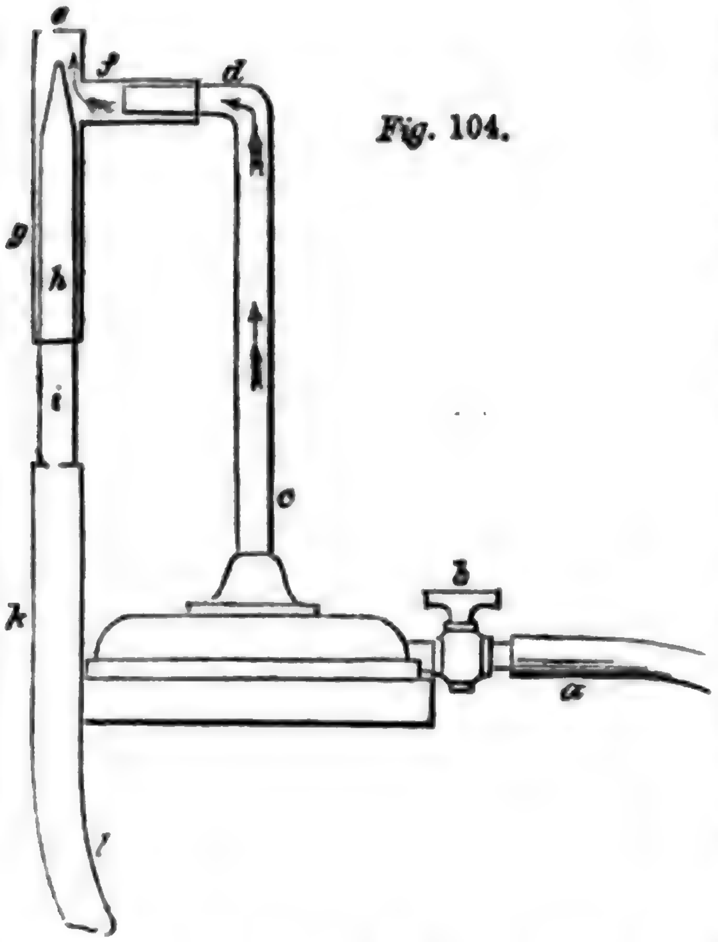
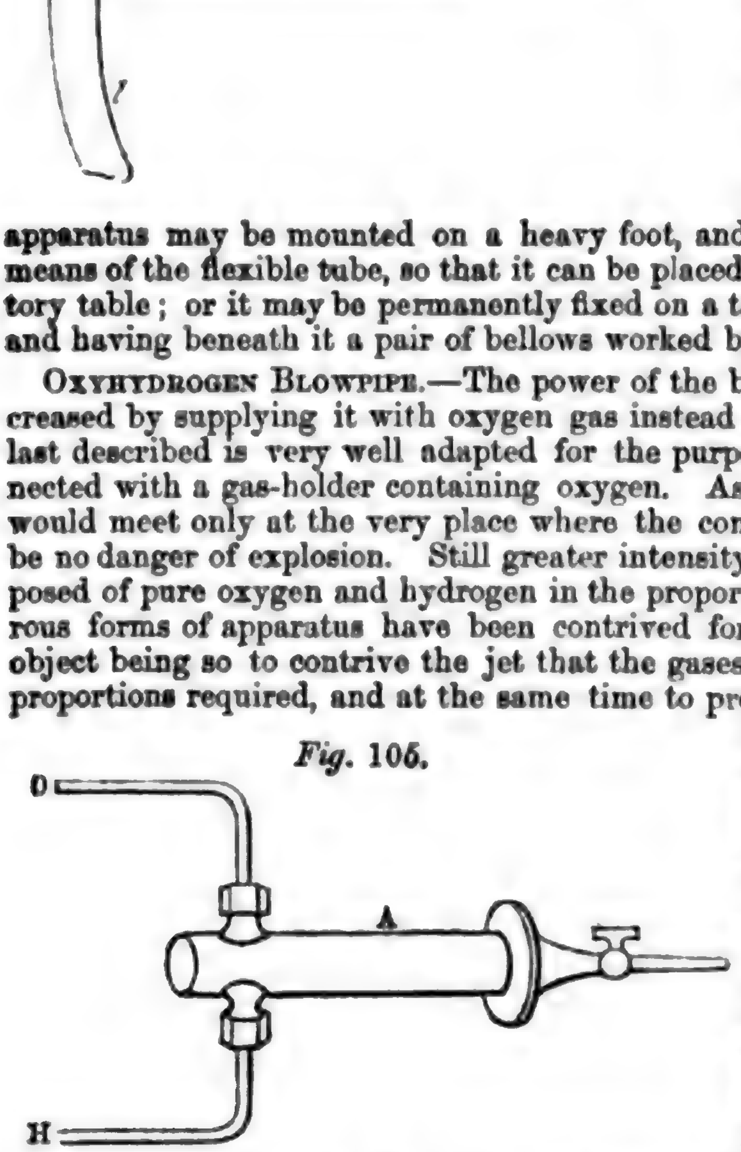


Fig. 104.

Table Blowpipe.—For sealing and bending glass tubes and constructing glass apparatus of various forms, it is convenient to have the blowpipe mounted on a fixed support, and when a flame of considerable power is required, the blast must be supplied by bellows worked with the foot. A very convenient form of blowpipe for these purposes is that invented by Herapath, and represented in *fig.* 104. *a* is a flexible tube attached to a stopcock *b*, which communicates with a tube *c d*, bent at right angles at *d*, where a T-shaped tube *e f g* slips on by means of the piece *f*. The blowpipe jet *h i* passes into the longer arm of the T-piece, and fits somewhat tightly; *k l* is a second piece of flexible tube terminating in a mouth-piece, or connected with a blowing apparatus. On turning on the gas, it passes in the direction marked by the arrows, and is to be inflamed at *e*. On blowing with the mouth, or by means of a pair of bellows into the tube *k l*, the ignited gas takes the form of a blowpipe flame of great power, the nature of which is entirely under control by means of the stopcock *b*, and also by regulating the quantity of air supplied through the tube *k l*. The T-shaped piece is moveable at *f*, so that the jet may be directed to any position. The apparatus may be mounted on a heavy foot, and connected with the gas-supply, by means of the flexible tube, so that it can be placed in any required position on the labotory table; or it may be permanently fixed on a table specially devoted to the purpose, and having beneath it a pair of bellows worked by a treadle.

Oxyhydrogen Blowpipe.—The power of the blowpipe flame may be immensely increased by supplying it with oxygen gas instead of atmospheric air. The apparatus last described is very well adapted for the purpose, the flexible tube *k l* being connected with a gas-holder containing oxygen. As the oxygen and the combustible gas would meet only at the very place where the combustion is to take place there would be no danger of explosion. Still greater intensity of heat is obtained by a flame composed of pure oxygen and hydrogen in the proportions required to form water. Numerous forms of apparatus have been contrived for burning this gaseous mixture, the object being so to contrive the jet that the gases shall be there mixed in the exact proportions required, and at the same time to prevent danger of explosion by premature mixture. The best form is that shown in *fig.* 105, in which A is a brass tube filled with a number of layers of wire gauze pressed closely together, or with a bundle of very thin brass wires placed parallel to the axis of the tube, and firmly wedged together by a stout conical wire driven into the middle, so as to form a collection of extremely narrow tubes. The gases are supplied by the tubes O H, connected with gas-holders or loaded caoutchouc bags, one containing oxygen the other hydrogen. To the other end of the brass tube A

Fig. 105.



is attached a jet, the extremity of which is formed of platinum. The gases mix in the tube A, and pass on through the meshes of the wire-gauze or the interstices between the thin brass wires to the point of the jet, where they are set on fire. The proportions in which the gases are supplied are regulated by stopcocks on the tubes O H. The appearance of the flame, which should be a very narrow cone of a pale blue colour, indicates when the right proportion is attained, and this having been once determined, the position of the stopcocks may be marked, so as to ensure the right proportion of the two gases in all future experiments. The use of the wire-gauze or bundle of thin wires in the tube A is to supply a mass of good conducting material, which shall prevent the flame from passing backwards through that tube (see Flame). The heat produced by the oxyhydrogen flame is the greatest that can be produced by any artificial means, except by the electric current. Thick platinum wires melt in it like wax in the flame of a candle. By itself, however, it gives but little light; but any non-volatile and incombustible solid substance held in it becomes intensely luminous. If the point of the flame be directed on the rounded edge of a cylinder of quick lime, a pure white light of dazzling brilliancy is produced, inferior only to the electric light. It is called the *Drummond light*, and has been used for lighthouses.

BLUE, PRUSSIAN. See Cyanides of Iron.

BLUE, SAXON. The best Saxon blue colour may be made with the following composition: mix one ounce of the best powdered indigo with four ounces of sulphuric acid in a glass bottle or flask, and digest it for an hour at the heat of boiling water, shaking the mixture at different times; then add 12 oz. of water, stir the whole well, and filter when cold. Poerner adds 1 oz. of good dry potash at the end of twenty-four hours, and lets this stand as much longer before diluting with water. The cloth should be prepared with alum and tartar.

BODENITE. A mineral related to allanite, discovered by Kerndt in the oligoclase between Boden and Mauersberg, near Marienberg in Saxony. Found only in ill-defined prisms [rhombic?] of 110° to 112°, without trace of cleavage. Hardness 6·5. Specific gravity 3·523. Reddish or blackish-brown. Streak dirty white. Opaque with vitreous lustre. When strongly heated, it exhibits incandescence like gadolinite. Fusible only on the acute edges. Decomposed by strong acids. Analysis gave: 26·12 SiO^2; 10·33 Al^4O^3; 12·04 Fe^2O; 17·44 Y^2O; 10·46 Ce^2O; 7·56 La^2O; 1·61 Mn^2O; 6·32 Ca^2O; 2·33 Mg^2O; 1·21 K^2O; 0·84 Na^2O; and 3·01 H^2O: whence may be deduced the formula $6(3M^2O.SiO^2) + 2Al^4O^3.SiO^2$, the water being regarded as basic. Associated with this mineral are found black amorphous grains of another mineral, *Maromontite*, containing the same elements, but not exhibiting incandescence when heated. (Kerndt, J. pr. Chem. xliii. 219, 228.)

BOG-BUTTER. A fatty substance found in the peat-bogs of Ireland. It was first examined by Luck (Ann. Ch. Pharm. liv. 125), afterwards more exactly by Brazier (Chem. Gaz. [1852], 375). It is very soluble in alcohol, and crystallises from the solution in a network of slender needles. It melts at 51° C. (Luck), the crude fat at 45°, but after repeated crystallisation from alcohol and then from ether, at 52° to 52·7° (Brazier). It gives off the odour of acrolein when heated. By saponification with potash, it yields an acid, *Butyrolimnodic acid* (Bogbuttersäure), to which Luck assigned the improbable formula $C^{33}H^{33}O^4$; but according to Brazier, this acid has the same composition as palmitic acid, $C^{32}H^{32}O^4$, or $C^{16}H^{32}O^2$, and melts at 53° C.

BOG-HEAD COAL. See Coal.

BOG-ORES. See Iron.

BOHEIC ACID. $C^7H^{10}O^6 = C^7H^8O^4.H^2.O^2$.—An acid occurring in small quantity in black tea, together with quercitannic acid (Rochleder, Ann. Ch. Pharm. lxiii. 202.) To prepare it, a decoction of black tea is precipitated at the boiling heat with acetate of lead; the filtered liquid is left to stand for twenty-four hours, and again filtered to separate a small sediment; the clear solution is mixed with a quantity of ammonia sufficient to neutralise the acid reaction; the yellow precipitate stirred up with absolute alcohol, and decomposed by sulphuretted hydrogen; and the filtrate left to evaporate in vacuo over oil of vitriol. The residue is dissolved in water, and the solution is left to evaporate in vacuo, then dried at 100° C., this treatment being repeated three times, and the residue finally left for three weeks in vacuo.

The acid when pulverised is of a pale yellow colour, like quercitannic acid. Melts at 100° C. into a mass which draws out into threads. It cakes together when exposed to the air, even for a few minutes, and deliquesces very quickly. Colours ferric hydrochlorate brown, without precipitation. Dissolves in all proportions in water and in alcohol.

By dry distillation, it yields a light charcoal, and a distillate which smells of acetic acid and blackens iron salts. The aqueous and alcoholic solutions decompose when evaporated in contact with the air. The acid is dibasic, the formula of its normal salts being $C^7H^8O^4.M^2.O^2$.

The *barium-salt*, $C^7H^8Ba^2O^6 + H^2O$, is obtained as a yellow precipitate by mixing the solution of the acid in aqueous alcohol, with a slight excess of baryta-water. The *normal lead-salt*, $C^7H^8Pb^2O^6 + H^2O$, is obtained by mixing the alcoholic solution of the acid, after concentration over potash in vacuo, with alcoholic acetate of lead, washing the precipitate with alcohol, and drying at 100° C. It is white, with a tinge of grey. A *basic lead-salt*, $C^7H^8Pb^2O^6.Pb^2O$, is obtained by precipitating the aqueous solution of the acid with an ammoniacal solution of acetate of lead. It forms an egg-yellow precipitate. (Rochleder.)

BOILING POINT. See HEAT.

BOLE. A massive mineral, having a perfectly conchoïdal fracture, a glimmering internal lustre, and a shining streak. Its colours are yellow-red, and brownish-black. It is translucent or opaque; soft, so as to be easily cut and to yield to the nail. It adheres to the tongue, has a greasy feel, and falls to pieces in water. Specific gravity 1·4 to 2. It may be polished. If it be immersed in water after it is dried, it falls asunder with a crackling noise. It is a hydrated silicate of aluminium, in which the aluminium is more or less replaced by iron (ferricum).

The following are analyses of bole:

	SiO^2	Al^4O^3	Fe^4O^3	Ca^2O	Mg^2O	K^2O	H^2O		
a. . .	41·9	20·9	12·2	—	—	—	24·9	= 99·9	(Wackenroder)
b. . .	42·00	24·04	10·03	0·52	0·43	—	24·03	= 101·05	(Löwig)
c. . .	41·05	25·03	8·09	0·45	0·50	—	24·02	= 99·14	„
d. . .	43·00	20·12	8·53	2·81	2·01	0·50	24·00	= 99·97	(Zellner)
e. . .	45·92	22·14	—	3·90	—	—	25·86	= 97·82	(Rammelsberg)
f. . .	47·03	18·46	6·36	1·00	—	0·90*	25·28	= 99·03	(Thomson)

a, from Säsebühl, near Göttingen; *b*, from Ettinghausen; *c*, from Cap de Prudelles; *d* from the Brechte Berg in Silesia. The composition of these specimens agrees nearly with the formula $4M^4O^3.9SiO^2.18H^2O$, which, by substituting $m = \frac{2}{3}M$, may be reduced to $m^8H^4Si^3O^{12} + 4aq$; *e*, from Stolpen in Saxony, is represented nearly by the formula $Ca^2O.2Al^4O^3.4SiO^2 + 4aq = (Ca^2al^{12}H^2)Si^4O^{16} + 3aq$; *f*, from the Giant's Causeway in Ireland, is nearly $M^4O^3.3SiO^2 + 6aq$, which may be reduced to $(m^2H^2)SiO^4 + aq$. All these are formulæ of orthosilicates. (*Rammelsberg's Mineralchemie*, 578; Dana, ii. 252.)

BOLOGNIAN STONE. Lemery reports that an Italian shoemaker, named Vincenzo Casciarolo, first discovered the phosphoric property of the Bolognian stone. It is the ponderous spar, or native sulphate of baryta. If it be first heated to ignition, then finely powdered, and made into a paste with mucilage, and this paste, divided into pieces a quarter of an inch thick, and dried in a moderate heat, be exposed to the heat of a wind furnace, by placing them loose in the midst of the charcoal, a pyrophorus will be obtained, which, after a few minutes' exposure to the sun's rays, will give light enough in the dark to render the figures on the dial-plate of a watch visible. U.

BOLETIC ACID. The name given by Braconnot to the acid existing in *Boletus pseudo-igniarius*, since shown by Bolley and Dessaignes to be identical with fumaric acid.

BOLETUS. A genus of mushroom, of which several species have been subjected to chemical examination by Braconnot and Bouillon La Grange (Ann. Chim. lxxx. 272); and more recently by Bolley, (Ann. Ch. Pharm. lxxxvi. 44), and Dessaignes (Compt. rend. xxxvii. 780).

The chief constituents of these fungi are extractive matter, nitrogenous principles, the so-called fungin (*q. v.*), sometimes mannite, perhaps also fermentable sugar and certain organic acids, called *fungic* and *boletic* acids by Braconnot, but probably consisting, according to Dessaignes, of malic or fumaric acid. The ash contains potash, lime, magnesia, phosphoric acid, &c. The species which have been examined are *Boletus bovinus* (Crell's Chem. Ann. 1785, p. 280), *B. igniarius* (Ann. Chim. li. 75), *B. juglandis* (*ibid.* lxxxvii. 226), *B. laricis* (*ibid.* lxxx. 272), *B. sulphureus* and *B. viscidus* (Trommsdorff's N. Journ. ix. 240).

Boletus laricis, is used on the continent in medicine under the name of *agaric*. It is in white, light, friable pieces, the outside of which is like dark-coloured leather. Its taste, at first sweetish, soon becomes bitter and acrid. Its infusion in water is yellowish, sweet tasted, and reddens vegetable blues.

Boletus igniarius is found in most countries, and particularly in the Highlands of Scotland, on the trunks of old ash and other trees. The French and Germans prepare it abundantly for making *tinder*, by boiling in water, drying, beating it, steeping it in a solution of nitre, and again drying it. In France it is called *amadou*, in this country *German tinder*. It has been recommended in surgery for stopping hæmorrhage from wounds. It imparts to water a deep brown colour and an astringent taste.

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* Chloride of sodium.

BOLORETIN. A resin of earthy aspect, found in the fossil fir-wood of Danish peat-bogs, and in the needles which fall from the growing trees. The fresh shoots contain but little of it; but it increases with the age of the needles, and is most abundant in autumn and winter. It is prepared by treating with boiling alcohol the grey earthy matter found in hollow fossil fir-stems, and precipitating the foreign matters with acetate of lead. The solution on cooling deposits the boloretin as an earthy mass, which may be further purified by repeated solution in boiling alcohol, with addition of hydrochloric acid to precipitate lead. It is soluble in ether, but not in cold alcohol. Melts at 75°—79° C. Its composition is variable, but it appears always to contain the elements of oil of turpentine *plus* water. It does not, however, yield oil of turpentine when treated with phosphoric anhydride. (Forchammer, Ann. Ch. Pharm. xli. 44.)

BOLTONITE. A variety of olivin, Mg^4SiO^4, occurring in crystalline granules, disseminated through limestone at Bolton in Massachussets. Colour ash-grey, wax-yellow, or yellowish-white, with vitreous lustre. Streak white. Transparent or translucent. Specific gravity 3·008 (Silliman); 3·21 (Brush). Hardness in unaltered specimens = 6 or rather greater (Brush). Cleavage distinct in one direction. Infusible before the blowpipe; slightly attacked by hydrochloric acid. The following analyses agree nearly with the formula Mg^4SiO^4 or $2Mg^2O.SiO^2$: *a* by J. L. Smith (Sill. Am. J. [2] xviii. 372); *b* by G. J. Brush (*ibid.* xxvii. 395):

	SiO^2	Mg^2O	Fe^2O	Ca^2O	Al^4O^3	Loss by ignition.	
a.	42·31	51·16	2·77	. .	0·18	1·90	= 98·32
b.	42·82	54·44	1·47	0·85	trace	0·76	= 100·43

Analyses by B. Silliman (Sill. Am. J. [2] viii. 15) and v. Hauer (Kenngott's Uebersicht, 1854, 90) gave larger amounts of silica and alumina, and less magnesia; but the mineral appears to have been but imperfectly decomposed.

BOLUS. A highly ferruginous clay from Sinope in Asia Minor, containing, according to Klaproth, 32·0 SiO^2, 26·5 Al^4O^3, 21·0 Fe^4O^3, 17·0 H^2O, and 1·5 NaCl.

BONE. (E. v. Bibra, Chemische Untersuchungen über die Knochen und Zähne, &c. Schweinfurt, 1844, p. 1—258, 289—385; E. Frémy, Ann. Ch. Phys. [3] xlvii. 47—107; also Traité de Chimie, par Pelouze et Frémy, 2nd edition, vi. 261; C. J. Lehmann, Physiological Chemistry, iii. 12, and Gmelin's Handbuch, viii. 429.)—Bone-tissue is of two kinds, *compact* and *spongy*. The long tubular bones of the extremities are formed mainly of the compact tissue, while the flat bones, as those of the skull and pelvis, and the short round bones, consist of an external compact layer, enclosing a mass of the more porous or spongy tissue. The outer surface of bones is covered with a thin membrane (the *periosteum*), traversed by great numbers of nerves and bloodvessels, while the inner surfaces of their cavities and channels are lined with a still thinner membrane. These tubes and cavities contain a fatty substance called *marrow*. The substance of the bone itself exhibits a laminated structure, the individual layers being concentric with the tubes and channels containing the marrow. These layers consist of an amorphous substance, intersected by cavities, from which proceed innumerable intercommunicating channels.

The true bony tissue, distinguished from the external and internal membranes, the marrow, and the various fluids contained in the channels and cavities above-mentioned, consists essentially of an organic substance, called *bone-cartilage*, or *ossein*, and an inorganic substance, composed mainly of *tribasic phosphate of calcium*, Ca^3PO^4, together with smaller quantities of *phosphate of magnesium*, Mg^3PO^4, *carbonate of calcium*, and *fluoride of calcium*.

If a bone be incinerated without previously reducing it to powder, and washing out the blood and other extraneous fluids contained in its cavities, the ash will likewise contain small quantities of *alkaline sulphates*, *carbonates*, and *chlorides*, and of *iron*, but these are derived from the liquids just mentioned, and do not properly belong to the bone itself.

The bone-cartilage or ossein may be separated from the earthy matter by macerating a bone for some time in dilute hydrochloric acid. The calcium-salts then gradually dissolve, the mass becomes translucent and soft, and ultimately the cartilage is left free from mineral matter, and retaining the form of the bone. By boiling in water, it is converted into gelatin and dissolves, forming a solution clouded by suspended fat and vascular tissue, and solidifying in a jelly on cooling. When freed from these extraneous matters by digestion in alcohol and in ether, it is found to have the same proportional constitution as gelatin, as may be seen from the following table, in which the composition of bone-cartilage from various sources is compared with that of pure gelatin (isinglass).

Composition of Gelatin and Bone-cartilage.

	Carbon.	Hydrogen.	Nitrogen.	Oxygen.	
Gelatin:					
From Bone	50·40	6·64	18·34	24·64	Mulder.
„ „ (fossil) . .	50·40	7·11	18·15	24·36	v. Bibra.
„ Isinglass . . .	50·76	6·64	18·32	24·69	Mulder.
Bone-cartilage:					
From femur of Ox . .	50·13	7·07	18·45	24·35	v. Bibra.
„ Pipa . .	50·45	7·08	18·21	24·24	„
„ Rib of River Carp .	50·32	7·22	18·42	24·00	„
„ Ox . . .	49·81	7·14	17·32	25·67	Frémy.
„ Calf . . .	49·9	7·3	17·2	25·6	„
„ Owl . . .	49·05	6·77			„

Bone-cartilage also contains sulphur, which v. Bibra estimates at 0·216 per cent.

The chief difference between bone-cartilage and gelatin is, that the latter dissolves easily and immediately in boiling water, whereas the former is insoluble in water until it has been converted into gelatin, which requires long boiling.

According to Frémy, the bone-cartilage has likewise the same composition in young and in old animals. Fœtal bones, however, do not appear to yield gelatin when boiled with water; or at all events, Schwann (Mikrosk. Unters. 1839, p. 3), could not obtain that substance from the bones of a fœtal calf, nor Hoppel (Arch. f. pathol. Anat. v. 174) from those of a rabbit, down to the last hours of intra-uterine life. In *fossil bones*, the cartilage is often found to be converted into true gelatin. The cartilage of diseased bones does not appear to differ from that of healthy bones (v. Bibra and others). In the bones of certain water-birds, and in the spines of certain fishes, Frémy found a substance resembling ossein in physical characters, and isomeric with it, but differing from it in not yielding gelatin when boiled with water.

Quantitative Analysis.—The bone is first reduced to fine powder by rasping, then washed with water to remove soluble salts, &c., and digested with ether to remove fatty matters. Care must however be taken not to continue the washing with water too long, as by the prolonged action of water, small quantities of the phosphates of calcium and magnesium are dissolved out, the quantity thus removed increasing as the organic matter of the bone passes more and more into the state of putrefaction. (Wöhler.)

The bone purified as above, is next incinerated in a muffle (p. 418), till it becomes quite white, then moistened with solution of carbonate of ammonium, to restore any carbonic acid that may have been driven off from the lime, and again heated just sufficiently to expel the excess of carbonate of ammonium. The difference between the weight of the dried bone before ignition, and that of the ash, gives the amount of cartilage.

The analysis of the ash is made for the most part by the ordinary methods (p. 419).

The *carbonic acid* must be estimated by one of the methods given under ALKALIMETRY (p. 117), first in the unignited bone-powder, and afterwards in the ash. The first gives the amount of carbonate of calcium in the bone, and from the difference of the two determinations, the quantity of lime which was in combination with organic acids may be found. The amount of carbonate of calcium cannot be correctly estimated by precipitating with carbonate of ammonium the lime which remains in solution after the phosphate of calcium has been precipitated by caustic ammonia. The adoption of this method in the earlier analyses, led to the incorrect conclusion that the calcium-phosphate contained in bone-earth was $8Ca^2O.P^2O^5$, instead of $3Ca^2O.P^2O^5$.

The amount of *fluorine* in bones has seldom been determined quantitatively, the calcium really existing as fluoride being generally reckoned together with the carbonate or phosphate. Marchand, however (J. pr. Chem. xxvii. 83), found in a human thigh-bone 1 per cent., and Heintz (Wien, Akad. Ber. 1849, p. 51), found in a similar bone 2·05 per cent. fluoride of calcium. In fossil bones, the proportion of this salt is often much greater.

As bone-tissue is very hygroscopic, it is necessary, in comparing the quantities of *water* which different bones retain, after drying in the air at ordinary temperatures, to notice the indications of the barometer and thermometer before exposing the bones to the heat of the water-bath or oil-bath.

The most complete investigations that have been made of the composition of bone, are those of v. Bibra and Frémy. The following table exhibits the percentage of inorganic matter in human bones of various ages, as determined by v. Bibra.

Name of Bone.	Percentage of Ash.	Name of Bone.	Percentage of Ash.
Male fœtus, 7 months:		*Woman*, 25 years:	
Femur, tibia, humerus	59·1 to 59·6	Femur, tibia, fibula, ulna, os occipitis	68·4 to 68·8
Female fœtus, 7 months	64·5 to 65·4	Humerus	69·25
Boy, 2 months:		Clavicule	67·51
Tibia	65·32	Rib	64·57
Atlas	64·07	Sternum	51·43
Boy, ¾ year:		Scapula	65·48
Femur	56·43	Vertebræ	54·25
Humerus	58·58	Os innominatum	59·97
Tibia	56·58	*Man*, between 25 and 30 yrs.	
Radius	52·52	Femur, tibia, humerus, ulna	68·0 to 69·4
Ulna	56·51	Os occipitis	68·73
Rib	49·30	Rib	63·99
Scapula	49·71	*Woman*, 78 years:	
Boy, 5 years:		Femur	66·81
Femur	67·80	*Man*, 58 years:	
Tibia	67·71	Femur, dense portion	68·53
Girl, 19 years:		,, spongy portion	64·18
Femur	67·85		
Humerus	67·71		

From these results it appears: 1. That the proportion of inorganic matter in bone is smaller in youth than in age, although no regular gradation can be observed. 2. The proportion of inorganic matter is greater in compact than in spongy bone-tissue; greater also in the bones of the extremities than in those of the trunk; greatest of all in the thigh-bone. It appears, indeed, to be greatest in those bones which are most moved, or have to bear the greatest strain; this observation is corroborated by the composition of the bones of birds (see below).

The different orders of mammiferous animals do not exhibit any essential differences in the proportions of inorganic matter in their bones, the limits being 64 and 75 per cent. The bones of birds contain on the average a larger proportion of inorganic matter than those of mammals, viz. 68·6 to 75·8 per cent.; those of reptiles rather less, 51·7 to 68·9 per cent. The bones of fishes exhibit great variety in the proportion of mineral matter which they contain, *e. g.* Bony fishes: *eel* 51·62 per cent.; *cod* 65·76; *salmon* 64·37; *perch* 59·40 per cent. Cartilaginous fishes: *Shark* 46·82 per cent.; *lamprey* 1·66 per cent.

Frémy's results agree for the most part with those of v. Bibra, excepting in the proportion of organic and inorganic matter in bones of different ages, which, according to Frémy, do not exhibit in this respect any sensible variation. The bone of a fœtus was found to yield the same quantity of ash as that of a woman 97 years of age, and the first bony particles that make their appearance in the midst of the cartilaginous mass, which in the fœtus precedes the formation of true bone, were found to contain the same quantity of mineral matter as the bone of an adult animal (see table, p. 621). The greater brittleness of the bones in age is attributed by Frémy to the increase in the proportion of the spongy tissue, the thickness of the hard and dense portion of the bones continually diminishing as age advances.

Frémy's analyses of the bones of animals belonging to different orders show, in accordance with those of v. Bibra, that the bones of mammifers exhibit the same average composition as those of man, the bones of herbivorous quadrupeds, however, generally containing a larger proportion of lime-salts than those of flesh-eaters. The bones of birds have nearly the same proportion of lime-salts as those of herbivorous mammals, and those of reptiles nearly the same as those of carnivorous mammals. The bones of fishes exhibit great diversity of composition, those of bony fishes being very much like those of mammifers, whereas those of cartilaginous fishes are rich in organic matter, and contain but a small proportion of mineral salts.

Comparative Analyses of Bones belonging to different Orders of the Animal Kingdom.
(Frémy.)

Name of Bone.	Ash per cent.	Phosphate of Calcium.	Phosphate of Magnesium.	Carbonate of Calcium.
Male fœtus, 4 months; femur	61·7	60·2		
„ 6 months; „	62·8	60·2		
Female fœtus, „	63·0			
„ 7 months; humerus	62·8			
Girl, born alive; femur	64·8	60·8		
Boy, 18 months; „	64·6	61·5		
Woman, 22 years; scapula	63·3	60·0		
„ „ cranium	64·1	57·8	1·7	10·9
„ „ femur	64·6			
„ „ humerus	64·1			
Man; spongy part of femur	61·0			
„ dense „ „	65·0			
Man, 40 years; femur	64·2	56·9	1·3	10·2
Woman, 80 „ „	64·6	60·9	1·2	7·5
„ 81 „ „	64·5	58·1	1·2	10·0
„ 88 „ „	64·3	57·4	1·2	9·3
„ „ spongy part of femur	59·7	54·0	1·2	7·0
„ 97 „ femur	64·9	57·0	1·2	9·3
Egyptian mummy; femur	65·0	58·7	1·7	5·9
Daki; femur	64·0			
Kinkajou; femur	62·0			
Genet	70·2			
Bitch; femur	62·1	59·0	1·2	6·1
Young lioness; femur	64·7	60·0	1·5	6·3
Panther; femur	65·6			
Morse	63·1	53·9	1·5	9·3
Rabbit; femur	66·3	58·7	1·1	6·3
Guinea-pig	71·8			
Indian elephant	66·8	62·2	1·2	5·6
Java rhinoceros	65·3	60·0	2·3	5·2
Horse; femur	70·4			
Calf, still-born; spongy part of femur	61·5	60·5	1·2	
„ „ dense „ „	64·4	59·4	1·7	5·2
„ 5 months; femur	69·1	61·2	1·2	8·4
Cow, full grown „	70·7			
„ old „	71·1			
„ „ „	71·3	62·5	2·7	7·9
Ox; humerus	70·4	61·4	1·7	8·6
„ „	70·2	62·4	1·7	7·9
Bull; femur	69·3	59·8	1·5	8·4
Lamb; „	67·7	60·7	1·5	8·1
Sheep; „	70·0	62·9	1·3	7·7
Goat; „	68·0	58·3	1·2	8·4
Cachalot „	62·9	51·9	0·5	10·6
Whale; spongy part	57·5			
Eagle	70·5	60·6	1·7	8·4
Vulture	66·2			
Owl (Grand Duke)	71·3	61·6	1·5	8·8
Ostrich; dense part	70·0			
„ spongy part	67·0			
Bustard	71·1			
Chicken	68·2	64·4	1·1	5·6
Turkey	67·7	63·8	1·2	5·6
Partridge	70·7	65·4		
Heron	70·6	62·5	1·5	10·2
Thrush	66·6	63·0		
Humming bird; bones of head	55·0			
„ „ „ limbs	59·0			

TABLE.—*continued.*

Name of Bone.	Ash per cent.	Phosphate of Calcium.	Phosphate of Magnesium.	Carbonate of Calcium.
Teal	73·5	68·4	1·3	5·6
Turtle; carapace	64·3	58·0	1·2	
Land tortoise; carapace	64·0	56·0	1·2	10·7
Crocodile; cutaneous bone	64·6	58·3	trace	9·7
Crocodile	64·0	58·3	0·5	7·7
Serpent	67·5			
Cod	61·3	55·1	1·3	7·0
Barbel	60·2			
Sole	54·0			
Shad	50·			
Carp	61·4	58·1	1·1	4·7
Pike	66·9	64·2	1·2	4·7
Eel	57·0	56·1	trace	2·2
Tetrodon; maxillary with teeth	76·0			
Diodon; spine of the skin	68·8			
Shark	62·6			
Ray; cartilage	30·0	27·7	trace	4·3
„ scales	65·3	64·4	trace	1·3
Lamprey; head with teeth	2·2			

Diseased Bones.—Bones are subject to several diseases, in nearly all of which the proportion of inorganic matter is found to diminish. In *caries*, the calcareous portion of the bone is destroyed, without alteration of the cartilage, the latter still yielding gelatin when boiled with water. In a carious femur, v. Bibra found the proportion of inorganic salts reduced to 38·3 per cent., and in a portion of astragalus, taken from the centre of the caries, it was only 18·5 per cent.—In *osteomalacia* and *rachitis*, the proportion of mineral matter sometimes diminishes to such an extent, that the bones bend under the weight of the body. Marchand found in the femur of a rachitic child 72·20 per cent, cartilage, 7·20 fat, 14·78 phosphate of calcium, 3·0 carbonate of calcium, 0·80 phosphate of magnesium, and 2·02 sulphate of calcium, chloride of sodium, iron (and loss). In the *osteomalacia* of adults, the tribasic phosphate of calcium is converted into $\frac{8}{3}$-phosphate, $8Ca^2O.3P^2O^5$ (Weber), and the bones sometimes contain a free acid. In this disease, and in the rachitis of children, the cartilage is frequently altered in character, so that it no longer yields gelatin when boiled with water. *Exostosis* is the formation of osseous tumours on the surface of bones; these tumours likewise contain an excess of cartilage. *Sclerosis* is the formation of cartilage, and ultimately of true bony tissue within the medullary cavities and canals of the bones, which thus become denser and almost like ivory. Here also the organic matter is generally in excess, and the carbonate of calcium is increased in proportion to the phosphate. In *osteoporosis*, which is a dilatation of the medullary cavities, &c., either from the excessive development of the medulla, or from the solvent action of fluids infused into the cavities, the mineral matter is also found to disappear more quickly than the organic matter.

Fossil Bones.—When a bone is exposed to the air or buried in the earth, the organic tissue gradually disappears, while the calcareous salts remain. In buried bones, the tissue likewise becomes incrusted with various substances derived from the surrounding soil, so that fossil bones often contain considerable quantities of carbonate, sulphate, and fluoride of calcium, silica, &c., according to the nature of the formation in which they are embedded. The proportion of carbonate of calcium sometimes amounts to 67 per cent. The silica is in the form of quartz, that is, in the modification which is insoluble in acids and in dilute alkalis. In some cases, the proportion of tricalcic phosphate remains nearly the same as in the original bone, whereas in others it is greatly diminished. The proportion of phosphate of magnesium does not vary greatly; it diminishes, however, to a certain extent when the phosphate of calcium is replaced by carbonate of calcium or by siliceous compounds. Many fossil bones still retain a portion of their cartilage, which is sometimes also converted into true gelatin.

Analyses of Various Fossil bones. (Frémy.)

	Ash per cent.	Phosphate of Calcium.	Phosphate of Magnesium.	Carbonate of Calcium.	Silica and Fluoride of Calcium.	Organic Matter.
Ox, from the caves of Oreston; metatarsal bone, external portion having the aspect of wood	80·74	71·1	1·5	11·8		10·3
Internal portion of the same, very friable	80·6	71·5	1·7	11·3		11·0
Spongy portion of the same .	84·2	63·3	1·2	5·2	17·2	8·0
Rhinoceros, from Sansan (Gers): vertebræ	83·4	59·0		41·3	2·6	trace
Ribs of the same.	83·1	66·8		27·5	1·4	trace
Hyena, from the caves of Kirkdale, long bone . . .	75·5	72·0	1·3	4·7		20·0
Rhinoceros; dorsal vertebræ .	69·5	25·7	0·4	57·5	8·5	
" " humerus. . .	73·0	32·4	0·4	64·0	6·2	
" " teeth . . .	90·4	65·2	0·7	13·8	14·5	
Mastodon; tusk	90·4	56·5	0·7	13·1	24·3	
Bear; dense part of bones . .	83·9	50·7	0·4	23·6	9·8	
" spongy part . . .	76·7	23·1	1·2	67·5	14·0	
Anoplotherium; caudal vertebra	84·0	53·1	0·4	20·4	19·4	
Tortoise; vertebræ . . .	87·0	61·1	0·7	10·6	18·6	

BONE-BLACK. *Animal black, Animal charcoal, Beinschwarz.*—A product obtained by heating bones to redness in close vessels. Large quantities of stinking gas, empyreumatic oil, and volatile alkaloïds, are then evolved, and there remains a black mass consisting of an intimate mixture of charcoal containing nitrogen, with the mineral matter of the bone, chiefly phosphate and carbonate of calcium. It possesses the power of abstracting many solid substances from their solutions, and is used on a very large scale as a decolorising agent in the refining of sugar. That it may possess this property in the highest degree, the preparation must be so conducted as to leave the largest possible quantity of carbon in the product, and at the same time to render it very porous. The air must therefore be carefully excluded during the ignition, and the heat must be regulated so as not to cause the mass to cake together or become agglutinated by the fusion of organic substances. The bones should be fresh; those which have lost much of their organic matter by putrefaction, either in the air or underground, do not yield a sufficient quantity of charcoal. They should be coarsely comminuted and boiled to free them from fat, which would melt and yield a very compact charcoal.

The yield of bone-black varies from 30 to 60 per cent. according to the composition of the bones. The long cylindrical bones of the extremities are best adapted for the purpose; they yield about 60 per cent of bone-black, containing 1 to 1¼ carbon to 9 pts. phosphate of calcium. Ribs, skulls, and vertebræ yield a smaller quantity, and not of good quality: hence it is better to use them for the preparation of gelatin.

The carbonisation of bones is performed either in iron cylinders, like those used in the distillation of coal, or in covered pots of cast-iron or crucible-ware, heated in a reverberatory furnace; the latter method yields the best charcoal, but the former is adopted when it is desired to collect the volatile products which are given off. (See BONE-OIL.) (For details and figures of machinery, see *Ure's Dictionary of Arts, Manufactures, and Mines*, i. 369; *Muspratt's Chemistry*, i. 315; *Handwörterbuch d. Chem.* 2te Aufl. ii. 767).

Bone-black is extensively used both as a decolorising and deodorising agent; it likewise removes lime and its salts from their aqueous solutions, and is accordingly used for the purification of highly calcareous waters. In the refining of sugar, it serves to free the syrup both from colouring matter and from lime. It decomposes many metallic salts, sometimes absorbing the oxides or metallic acids, sometimes reducing them. It abstracts iodine, not only from solution, but even from its salts. It likewise removes bitter principles and organic alkaloïds from their solutions, and has been recommended as an antidote in case of poisoning by such substances.

Bone-black which has been used for removing colouring matter and lime from syrup or other liquids, may be *revivified*, that is, restored to its original state, by the following processes:—1. Treating it with acids to remove the lime.—2. Leaving it to ferment or putrefy, in order to render soluble the organic substances which it has absorbed.—3. Washing.—4. Ignition. (For details, see the works above cited.)

Bone-black is sometimes used as a pigment; for which purpose it is made into a paste with water, and finely pulverised in a colour-mill. The finest pigment of this kind is *ivory-black*, which is obtained by the carbonisation of ivory.

Lastly bone-black is used as a manure, especially for cereal crops, being well adapted for this purpose, both by the phosphoric acid and the nitrogen which it contains. It is chiefly efficacious on soils which still retain a considerable quantity of decayed vegetable matter.

BONE-OIL. *Dippel's oil, Animal oil, Oleum animale Dippelii.*—This oil is obtained in large quantity in the preparation of bone-black, by igniting charcoal in cylinders. Similar products are obtained by the dry distillation of other animal substances. The original *Dippel's oil* known in Pharmacy was produced from stag's horn; but all the animal oil now met with in commerce, is obtained from bones in the manner abovementioned. It has been made the subject of a series of elaborate investigations by Professor Anderson of Glasgow. (Transactions of the Royal Society of Edinburgh, xvi. 4; xx. Part II. 247; xxi. Part I. 219, and Part IV. 571. Ann. Ch. Pharm. lxx. 32; lxxx. 44; xciv. 358; cv. 335. Jahresber. f. Chem. 1847–8, p. 651; 1851, p. 475; 1854, p. 488; 1867, p. 392.)

Bone-oil is mainly a product of the decomposition of gelatinous tissue, inasmuch as the bones used for the preparation of animal charcoal are boiled, before ignition, with a large quantity of water, to deprive them of their fat (p. 624). The crude oil is dark brown or nearly black, and has a specific gravity of 0·970. It consists chiefly of a mixture of volatile organic bases, together with smaller quantities of acids and neutral hydrocarbons.

On subjecting a large quantity of the crude oil to fractional distillation, the first $\frac{2}{5}$ of the distillate consists of about equal parts of a yellow oil and a watery liquid holding in solution sulphide, cyanide, and carbonate of ammonium, together with small quantities of very volatile organic bases. On supersaturating this watery liquid with sulphuric acid, boiling for a while, then distilling with slaked lime, and immersing sticks of potash in the watery distillate, ammonia is given off with brisk effervescence, and a small quantity of oily bases separates on the surface of the potash-solution.

The remaining $\frac{3}{5}$ of the distillate consists of oily bases of various degrees of volatility. On mixing them (together with the small portion of oily bases separated from the watery liquid just mentioned) with excess of dilute sulphuric acid, setting the mixture aside for some days, and frequently shaking it, then separating the strongly acid liquid from the portion of oil still unacted on, and boiling it for some time in a still, an alkaline liquid passes over containing *pyrrhol*, C^4H^5N, a weak base first noticed by Runge (Pogg. Ann. xxxi. 65) in bone-oil and in coal-tar, and distinguished by the property of imparting a deep purple-red colour to fir wood moistened with hydrochloric acid.

The remaining acid liquid, after cooling, is mixed with excess of slaked lime and distilled, and the distillate is treated with solid caustic potash, which separates a quantity of oily bases, while the watery liquid retains in solution *ammonia* and *methylamine*, which are given off on simply distilling the liquid, and may be condensed in dilute hydrochloric acid.

On submitting to fractional distillation the mixture of oily bases separated by the potash, a number of bases are obtained from 65° to 100° C. belonging to the series $C^nH^{2n+3}N$, viz. ethylamine C^2H^7N, tritylamine C^3H^9N, tetrylamine $C^4H^{11}N$, and amylamine $C^5H^{13}H$; and above 115° C. another series of bases are given off belonging to the series $C^nH^{2n-5}N$, and isomeric with phenylamine and its homologues, viz.:

Pyridine, C^5H^5N, boiling at 116·7° C.
Picoline, C^6H^7N, „ „ 135
Lutidine, C^7H^9N, „ „ 154·5
Collidine, $C^8H^{11}N$, „ „ 180

The non-basic portion of bone-oil yields by repeated rectification, a liquid boiling at 65·5° C., which, when exposed to a freezing mixture, separates into two distinct layers. The portions boiling at a higher temperature do not exhibit this property. They contain *benzene*, and probably also homologues thereof, also *alcohol-radicles*, and *nitrogenous compounds* which are decomposed by sodium.

BONSDORFFITE. A variety of hydrous dichroïte (ii. 422).

BORACITE. *Borazite. Borate of Magnesia.*—A mineral occurring in crystals imbedded in gypsum and anhydrite at Lüneberg in Hanover, Segeberg in Holstein, and Luneville, La Meurthe, in France. The crystals are monometric; cubes, rhomboïdal dodecahedrons or tetrahedrons, generally hemihedral combinations with a great number of faces. Cleavage octahedral in traces. Specific gravity = 2·974. Hardness = 7. Lustre vitreous, inclining to adamantine. Colour white, inclining to grey, yellow, and green. Streak white. Subtransparent to subtranslucent. Fracture conchoïdal, uneven. Pyro-electric, even when massive. (Dana, ii. 393.)

Boracite was formerly regarded as a borate of magnesium, $3Mg^2O.B^2O^3$, containing a small quantity of iron; but recent analyses have shown that it likewise contains chlorine. The mean results are as follows:

Mg^2O	Fe^2O	B^2O^3	Cl	H^2O	
30·67	1·62	62·55	7·96	0·75	(Potyka.)
30·48	1·38	—	8·50	—	(Siewert and Geist.)

If now the ferrous oxide be reckoned as magnesia ($Fe^2O : Mg^2O = 72 : 40$) these analyses give respectively 31·57 and 31·25 magnesia; and the results agree nearly with the formula $MgCl.(3Mg^2O.4B^2O^3)$, which requires 31·35 per cent. Mg^2O, 62·50 B^2O^3, and 7·94 Cl. (Rammelsberg's Mineralchemie, p. 254.)

BORAX. Acid borate of sodium. See Borates, under Boron, Oxide of (p. 645).

BORIDES. Compounds of boron with metals. See Boron.

BORNEENE. *Valerene.* $C^{10}H^{16}$.—A liquid hydrocarbon, isomeric with oil of turpentine, secreted by the *Dryabalanops camphora,* and holding in solution a solid substance, borneol, or camphor of Borneo. It is also obtained from essential oil of valerian, by submitting that oil to fractional distillation, and heating the first portions of the distillate with hydrate of potassium, which takes up valerol, while borneene passes as a distillate. Solid Bornean camphor distilled with phosphoric anhydride also yields a liquid hydrocarbon having the composition $C^{10}H^{16}$. (See Valerian, Oil of.)

Borneene is lighter than water, almost insoluble in that liquid, and smells like oil of turpentine. It turns the plane of polarisation of a luminous ray to the left, but less strongly than oil of turpentine. The product obtained from oil of valerian boils at 160° C., that from Borneo camphor at 165°. Vapour-density 4·60. It absorbs hydrochloric acid gas, forming a cyrstalline compound. It appears to oxidise when left in badly closed vessels, and when immersed in water, especially in presence of alkalis, it appears to be converted into borneol (Gerhardt, Traité, iii. 628, 641). (See Dryabalanops.)

Borneene from Madder Fusel-oil.—The fusel-oil contained in the alcohol produced by the distillation of madder-sugar, yields liquid products when distilled at temperatures rising to 230° C., while at higher temperatures lævo-rotatory borneol sublimes. The former, by digestion with caustic potash, then with chloride of calcium, and repeated fractional distillation, yields a liquid which boils at 160° C., contains 88·23 per cent. carbon and 11·81 hydrogen, has a vapour-density = 4·85, and is therefore probably borneene. Lævo-rotatory borneol (*vid. inf.*) distilled with phosphoric anhydride also yields a liquid which appears to be borneene. (Jeanjean, Ann. Ch. Pharm. ci. 94.)

BORNEOL. *Borneol Alcohol, Solid Camphor of Borneo.* $C^{10}H^{18}O$.—This substance is extracted from the *Dryabalanops camphora,* being found in cavities in the trunks of old trees. It is also found in small quantity in moist oil of valerian, being probably formed by hydration of borneene.

According to Pierlot (Ann. Ch. Phys. ix. 291) the crystals found in oil of valerian are not borneol, but valerian-camphor, $C^{12}H^{20}$.

Borneol is produced artificially by heating common camphor with alcoholic potash, its formation being attended, either with evolution of oxygen:

$$\underset{\text{Camphor.}}{C^{10}H^{16}O} + H^2O = \underset{\text{Borneol.}}{C^{10}H^{18}O} + O;$$

or with simultaneous production of camphic acid:

$$\underset{\text{Camphor.}}{2C^{10}H^{16}O} + H^2O = \underset{\text{Borneol.}}{C^{10}H^{18}O} + \underset{\text{Camphic acid.}}{C^{10}H^{16}O^2}.$$

The action takes place slowly at 100° C., more quickly at higher temperatures in sealed tubes. (Berthelot, Ann. Ch. Phys. [3] lvi. 78.)

Borneol forms small transparent, colourless, very friable crystals or crystalline fragments, having an odour like that of common camphor and of pepper, and a hot burning taste. The crystals appear to be regular six-sided prisms belonging to the hexagonal system. Their alcoholic solution possesses dextro-rotatory power, like that of common camphor. Dextro-rotatory power of natural borneol = 33·40 (Biot), of the artificial = 44·9°. Borneol is lighter than water, and insoluble in that liquid, but very soluble in alcohol and ether. Melts at 198° C., and boils at 212°, distilling without alteration. Gently heated with phosphoric anhydride, it yields borneene, $C^{10}H^{16}$. Boiled with strong nitric acid, it gives off H^2, and is converted into common camphor, $C^{10}H^{16}O$. With hydrochloric acid it unites without liquefying: the compound is destroyed by heat.

Lævo-rotatory Borneol.—This substance, which is isomeric with ordinary borneol, but differs from it in possessing equal but opposite rotatory power, is found in the alcohol produced by the fermentation of madder-sugar, and is obtained by collecting the laminæ which crystallise out on standing, or during fractional distillation. It forms crystalline laminæ, or a white powder smelling like pepper and common camphor. It dissolves sparingly in water, and when thrown on the surface of water, spins like common camphor. It dissolves easily in acetic acid, alcohol, and ether. Boiling nitric acid converts it into lævo-rotatory camphor. Distilled with phosphoric anhydride or chloride of zinc, it yields a hydrocarbon resembling oil of lemon or bergamot. (Jeanjean, Ann. Ch. Pharm. ci. 94.)

BORNITE. Syn. with ERUBESCITE and with TETRADYMITE.

BOROCALCITE. Native borate of calcium (p. 643).

BORON. *Atomic Weight* 11. *Symbol* B.—This element occurs in nature as *boric* or *boracic acid*, and in a few minerals, viz. *native borax* or *tincal*, *boracite*, *hydroboracite*, *datolite*, and *botryolite*, and in small quantities in *schorl*, *apyrite*, *axinite*, and *rhodizite*. It never occurs in the free state. Homberg, in 1702, first obtained boric acid from borax, and anhydrous boric acid was decomposed by Gay-Lussac and Thènard in 1808, and immediately afterwards, by Sir H. Davy, into oxygen and boron.

Boron may be obtained in three different states, viz. *amorphous*, *graphitoïdal*, and *adamantine*. (Wöhler and Deville, Ann. Ch. Phys. [3] lii. 63.)

1. *Amorphous Boron.*—This is the form in which boron was first obtained. Gay-Lussac and Thénard prepared it by igniting boric anhydride (vitrefied boric acid) in a tube with an equal weight of potassium in small pieces, then boiling the fused mass with very dilute hydrochloric acid, washing with water, and drying. This process yields, however, but a small product, as it is difficult to deprive the boric acid of all its water, and the remaining quantity oxidises part of the potassium, with violent combustion, causing part of the mass to be projected. According to R. D. Thomson (Phil. Mag. [3] x. 419), this inconvenience may be obviated by drying the boric anhydride as completely as possible, mixing it in the state of coarse powder, with twice its weight of potassium, freed as completely as possible from the crust of hydrate which generally adheres to it, and gradually heating the mixture to redness in a glass tube over a lamp. Wöhler and Deville mix 60 grammes of sodium in small pieces with 100 grammes of finely powdered boric anhydride in an iron crucible, and cover the mixture with about 30 grammes of pulverised and previously ignited chloride of sodium. The crucible is then quickly heated to redness, whereupon a violent reaction takes place, and the whole becomes liquid. It is carefully stirred with an iron rod till no more free sodium or unfused chloride of sodium can be seen, then carefully poured into water acidulated with hydrochloric acid, and washed and dried as above. As the amorphous boron is very apt to run through the filter when washed with pure water, it is best to wash with water containing sal-ammoniac, and then remove that salt by means of alcohol.—Another mode of preparing amorphous boron is that of Berzelius, which consists in decomposing perfectly dry borofluoride of potassium by heating it with an equal weight of metallic potassium in an iron tube closed at both ends. The mixture is first heated merely to the melting point of potassium, then well stirred with an iron rod, and afterwards heated to redness. The decomposition takes place without explosion, and the boron is afterwards separated from the fluoride of potassium, with which it is mixed, by digestion and washing with water containing sal-ammoniac, the latter being finally removed by alcohol. If too little potassium has been taken to produce complete decomposition, the washing is rendered difficult by the remaining borofluoride of potassium, which has but little solubility. Amorphous boron is also formed, together with the other two varieties, in the modes of preparation presently to be described.

Amorphous boron is a dark-brown or greenish-brown powder, opaque, destitute of taste and smell, and stains the fingers strongly. It is a non-conductor of electricity. In vacuo, or in gases with which it does not unite, it may be raised even to a white heat without melting, or subliming, or undergoing any alteration, excepting that it becomes so dense that it sinks rapidly in oil of vitriol. In the unignited state, it dissolves, to a very slight extent, in pure water, imparting its colour; in water containing acids or salts it is insoluble, and indeed such substances precipitate it from its aqueous solution.

Amorphous boron does not oxidise in the air or in oxygen gas at ordinary temperatures, but at about 300° C. it burns in the air with a reddish light, and in oxygen gas with dazzling brightness; the combustion is in both cases attended with vivid emission of sparks, and in oxygen gas, according to Berzelius, a faint greenish flame is observed. The product is boric oxide or anhydride, B^2O^3, the only known oxide of boron, which melts on the surface of the boron and partly protects it from further action. In atmospheric air, according to Wöhler and Deville, a small quantity of nitride of boron is formed at the same time.

Amorphous boron does not decompose water, even at the boiling heat, but it readily decomposes strong sulphuric acid when heated with it, and nitric acid, even when but slightly concentrated, in the cold, the product in each case being boric acid. At a red heat, it decomposes the carbonates, sulphites, sulphates, nitrites, and nitrates of the alkali-metals, an alkaline borate being formed, and carbon, sulphur, or nitrogen set free. The decomposition is sometimes attended with incandescence and, in the case of nitre, with explosion. It also decomposes many metallic oxides at a red heat, forming a borate, if the oxide is in excess. Heated with hydrate of potassium, it eliminates hydrogen, and forms borate of potassium. It likewise reduces many metallic chlorides and sulphides, *e.g.* chloride of lead, chloride of silver, and sulphide of lead at a red heat, chloride of boron being formed and escaping as gas (Wöhler and Deville). It precipitates metallic gold from a solution of the chloride. When strongly ignited in a current of nitrogen gas, it is converted into white nitride of boron. Heated nearly to redness in a current of nitric oxide gas, it burns brilliantly, forming boric anhydride and nitride of boron. It does not decompose nitrous oxide. (Wöhler and Deville).

By ignition with aluminium, amorphous boron may be converted into the two other modifications, which remain behind on dissolving out the aluminium by hydrochloric acid.

Graphitoïdal Boron.—This variety of boron is obtained:—1. By passing gaseous chloride of boron for some time over aluminium in the state of fusion. The metal takes up but a small quantity of boron; but on breaking it, the boron is found on the fractured surface in copper-coloured crystalline laminæ, like graphite in cast-iron; they may be separated by dissolving out the aluminium with hydrochloric acid.—2. By heating 8 pts. of borofluoride of potassium and 5 pts. of aluminium with a flux of 9 pts. chloride of potassium and 7 pts. chloride of sodium to the melting point of silver, in a porcelain crucible, and treating the half fused metallic mass found in the midst of the slag, first with hydrochloric then with hydrofluoric acid. Boron then remains in small blackish-grey crystalline scales.—3. By fusing a mixture of 15 pts. boric anhydride, 10 pts. fluor-spar, and 2 pts. aluminium; or by fusing aluminium with boric anhydride, or better with fused borax and cryolite, and a flux of chloride of potassium and chloride of sodium. A large excess of aluminium, however, is required to obtain but a small quantity of boron.

Graphitoïdal boron has a semi-metallic lustre, like graphite or crystalline ferric oxide, but with a distinct tinge of copper-red. When well crystallised, it forms thin six-sided tablets belonging to the hexagonal system; but it is more generally obtained as a reddish-grey, micaceous powder composed of fine crystalline laminæ. It is perfectly opaque. When heated to redness in the air, it does not burn or undergo any apparent alteration. It does not dissolve in acids or in alkalis, but appears to be converted into boric acid by the long-continued action of nitric acid. (Wöhler and Deville.)

Adamantine or *Diamond Boron.*—This is not, strictly speaking, a form of pure boron; at least, as hitherto obtained, it always contains carbon and sometimes aluminium. To prepare it, 80 grammes of aluminium in lumps are heated with 100 grammes of boric anhydride to a temperature at which nickel fuses readily. The mixture is introduced into a crucible of compact charcoal fitted with a charcoal cover and placed within a hessian or black-lead crucible, the intermediate space being filled with charcoal-powder, and the cover fastened on with refractory luting; and the whole is exposed for five or six hours to the strongest heat of an air-furnace, having a tall chimney and fed with a mixture of coke and coal. On breaking the crucible after cooling, two layers are found, one glassy, consisting of boric anhydride and alumina, the other a metallic iron-grey mass of aluminium, penetrated throughout with crystalline boron. The aluminium is dissolved out by strong soda-ley, iron by hot hydrochloric acid, and the residue is treated with a hot mixture of nitric and hydrofluoric acid, to remove silicium. The crystals of diamond boron thus far purified are still mixed with graphitoïdal boron and crystalline laminæ of alumina; the former, being light, may be separated by levigation; the latter only by careful mechanical selection.

Adamantine boron forms quadratic octahedrons, in which the principal axis is to the secondary axes as 0·577 : 1. The crystals vary in colour, from a scarcely perceptible honey-yellow to deep garnet-red; sometimes they are so deeply coloured, probably by amorphous boron, that they appear black. In lustre and refracting power, they are nearly equal to the diamond. Their specific gravity is 2·63. They are extremely hard, always sufficiently so to scratch corundum with facility, and some crystals are nearly as hard as diamond itself. The hardest are obtained by repeatedly exposing aluminium to the action of boric anhydride at a temperature high enough to cause the anhydride to volatilise very quickly.

Adamantine boron does not fuse, even at the heat of the oxyhydrogen blowpipe, and withstands the action of oxygen even when very strongly heated; but it is slightly oxidised at the temperature at which the diamond burns, a film of boric anhydride being then formed, which stops further oxidation. Heated on platinum-foil before the blowpipe, it forms a fusible boride of platinum. It is not attacked by acids at any temperature, but when heated to redness with acid sulphate of potassium, it is converted into boric acid. It is not attacked by a strong boiling solution of caustic soda, but is slowly dissolved by hydrate or carbonate of sodium at a red heat. Nitre does not appear to act upon it at any temperature.

Boron unites, as already observed, with oxygen and with nitrogen, also with chlorine, bromine, fluorine, and sulphur. With metals it does not, for the most part, unite readily; but borides of palladium and platinum are known. The platinum compound is very fusible, so that boron, in either of its modifications, if ignited on platinum-foil before the blowpipe, instantly perforates the platinum. (Wöhler and Deville.)

Boron in all its combinations appears to be triatomic; the chloride being BCl^3, the oxide B^2O^3, the hydrate (boric acid) H^3BO^3, &c.

BORON, BROMIDE OF. BBr^3.—Discovered by Poggiale in 1846 (Compt. rend. xxii. 124), but first obtained pure by Wöhler and Deville (Ann. Ch. Phys. [3] lii. 89.) It is produced by the action of bromine on amorphous boron, or on boric anhydride in presence of charcoal. The best way of preparing it is to pass bromine-vapour over heated amorphous boron, previously well dried in a current of hydrogen; then digest the product for some time with metallic mercury, to remove excess of bromine, and distil.

Pure bromide of boron is a colourless mobile liquid, of specific gravity 2·69, volatilising readily at ordinary temperatures, in colourless, pungent vapours, and boiling under the ordinary atmospheric pressure, at 90° C. Vapour-density (referred to air), by experiment, 8·78; by calculation (2 vol.) = 8·7. It fumes in moist air, and is instantly decomposed by water, with formation of boric and hydrobromic acids. With dry ammonia-gas, it forms a white pulverulent substance, which is converted by water into bromide and borate of ammonium: possibly thus:

$$BBr^3.4NH^3 + 2H^2O = 3NH^4Br + NH^4BO^2.$$

BORON, CHLORIDE OF. BCl^3.—First prepared by Berzelius (Pogg. Ann. ii. 147), afterwards by Dumas (Ann. Ch. Phys. [2] xxxi. 436; xxxiii. 376), more exactly investigated by Wöhler and Deville (*ibid.* [3] lii. 88). It is formed by the direct combination of chlorine and boron, which takes place at ordinary temperatures, or at a gentle heat; also by heating boron in hydrochloric acid gas, or a mixture of boric anhydride and charcoal in chlorine gas, and by the action of boron at a red heat on chloride of mercury, lead, or silver.

To prepare it, amorphous boron, loosely packed in a glass tube, is first freed from moisture by passing dry hydrogen over it at a gentle heat; the tube is then left open for a few seconds, to allow the hydrogen to escape; after which, dry chlorine gas is passed through the tube, the action being assisted if necessary, by gently heating the tube in a combustion furnace. Combination then takes place, attended with evolution of light and heat; and the vapours of chloride of boron are passed through a caoutchouc connecting-tube into a Y-shaped tube, the two upper arms of which are surrounded with ice and salt, while the lower arm conveys the condensed liquid into a receiver placed below. The product may be freed from excess of chlorine by digestion with mercury. A small quantity of oxychloride of boron is generally formed at the same time, by the action of a little air or moisture left in the apparatus; but it condenses in the cooler part of the combustion-tube. The chloride of boron may be freed from excess of chlorine by digestion with mercury.

When the vapour of chloride of boron is mixed with hydrogen, as when it is produced by heating boron in hydrochloric acid gas, or with carbonic oxide, as when produced by the action of chlorine on a hot mixture of boric anhydride and charcoal, it is very difficult to condense; indeed, chloride of boron was originally regarded as a gas at ordinary temperatures, until Wöhler and Deville obtained it in a state of purity by the process above described.

Pure chloride of boron is a colourless, mobile, strongly refracting liquid, having a specific gravity of 1·35 at 17° C. (? 7°); it expands very perceptibly by a rise of 1° or 2° of temperature. It boils at 17° C. Vapour-density, by experiment = 4·06—4·08; by calculation (2 vol.) = 4·07. It fumes in damp air, and is quickly decomposed by water, yielding boric and hydrochloric acids. With alcohol, it forms, with great rise of temperature, hydrochloric acid and borate of ethyl: similar reactions with methylic and amylic alcohols.

Ammonio-chloride of Boron, $3NH^3.2BCl^3$, is formed, with great evolution of heat, when dry ammonia-gas is passed over chloride of boron. It is a white, finely crystalline powder, which sublimes unaltered when heated alone, though not so easily as sal-ammoniac. It does not fume in the air, but is decomposed by water, yielding boric acid, chloride of ammonium, and hydrochloric acid:

$$2BCl^3.3NH^3 + 6H^2O = 2H^3BO^3 + 3NH^4Cl + 3HCl.$$

When the vapour of this compound, mixed with ammonia-gas, is passed through a red-hot tube, nitride of boron is produced.

BORON, CHLOROCYANIDE OF. See CYANOGEN, CHLORIDE OF.

BORON, DETECTION AND ESTIMATION OF. Boron almost always occurs in the form of boric acid, and therefore the reactions by which it is detected are best considered in detail in connection with that acid (see page 639). When the acid is in the free state, it is easily recognised by the green colour which it imparts to flame, especially to an alcohol flame, and by its peculiar action on turmeric paper. If the acid is in combination with a base, the compound must first be decomposed in the state of powder by sulphuric acid, and the boric acid extracted with alcohol. Native borates not decomposible by sulphuric acid, must be fused with potash, and then digested with alcohol and sulphuric acid. Another method of detecting boron in minerals is to mix the pulverised substance with 4 pts. of a flux containing 1 pt. pounded fluorspar and 4½ pts. acid sulphate of potassium, made into a paste with a little water, and heat the mixture on a platinum wire in the inner blowpipe flame. As the mass melts, fluoride of boron is given off, and imparts a yellow-green colour to the outer flame. If the quantity of boron present is small, this appearance lasts only for a few seconds, ceasing, in fact, as soon as the fluoride of boron is completely volatilised.

The green colour imparted to flame is a very delicate test for boron. Before applying it, however, care must be taken to ensure the complete absence of copper, as the salts of this metal impart a very bright green colour to flame. Certain chlorine-compounds also colour flames green, as when hydrochloric acid is dropped into an alcohol flame; but the green colour thus produced has a decided bluish tinge, which distinguishes it from that produced by boron. Lastly, phosphates moistened with sulphuric acid, also give a faint green colour to the outer blowpipe flame.

Quantitative Estimation.—The exact estimation of boron presents considerable difficulties, as all borates are more or less soluble in water or in alcohol, and boric acid cannot be heated without loss in contact with water. The best mode of direct estimation, originally proposed by Berzelius, and perfected by Stromeyer (Ann. Ch. Pharm. c. 82), is to precipitate the boron as borofluoride of potassium, which is quite insoluble in alcohol of a certain strength. This mode of precipitation, however, is directly applicable only when the boron exists in solution as borate of potassium: any other bases present must first be separated. Borates of the alkaline-earth-metals, earth-metals, or heavy metals, are fused with carbonate of potassium; and the mass is digested in water, which takes up nothing but borate of potassium, except perhaps a trace of magnesia. Borate of sodium is treated with alcohol and sulphuric acid; the alcoholic liquid filtered from the sulphate of sodium, is mixed with excess of potash free from silicic and carbonic acids; and the alcohol is evaporated. The alkaline borate of potassium obtained in either case, is now to be saturated with pure hydrofluoric acid, and the liquid evaporated to dryness in a silver or platinum vessel; the dry saline mass is macerated with a solution of acetate of potassium (1 pt. of the salt to 4 pts. water); the undissolved borofluoride of potassium is collected on a weighed filter supported on a gutta-percha funnel, and washed, first with the solution of acetate of potassium, which removes chloride, phosphate, and sulphate of potassium, likewise sodium-salts though slowly, and afterwards with alcohol of 84 per cent. Tralles (specific gravity 0·8526), then dried at 100° C. and weighed. 100 parts of the borofluoride correspond to 27·78 boric anhydride, or 9·06 boron.

To ascertain whether the precipitate is pure, it is dissolved in boiling water, which leaves behind any traces of magnesia that may be present, and the solution is treated with ammonia, which precipitates silica if present: the precipitate may then be washed, first with acetate of potassium, then with alcohol, and its weight ascertained.

The quantity of free boric acid in an aqueous or alcoholic solution, cannot be determined by evaporation to dryness, because a considerable quantity of the acid goes off with the aqueous or alcoholic vapours: even the presence of excess of lead-oxide, baryta, or basic phosphate of sodium, does not completely prevent this evaporation. Ammonia prevents the volatilisation to a greater extent than either of these substances, but it does not quite prevent loss. The only exact mode of determining boric acid by evaporation, is to supersaturate the liquid with a known weight of pure fused carbonate of sodium (about 2 pts. of the carbonate to 1 pt. of acid supposed to be present); then evaporate to dryness, and ignite the residue in a covered crucible. The amount of carbonic anhydride in the residue is then to be determined by the method given under ALKALIMETRY (p. 149), and deducting this, together with the known weight of soda contained in the carbonate added, from the total weight of the residue, the remainder is the quantity of boric anhydride present.

Boron in borates may be estimated *indirectly* in several ways. The best method is to digest a weighed quantity of the pulverised compound in a capacious platinum crucible, with hydrofluoric acid, then gradually add strong sulphuric acid, and heat the mixture, gently at first, and afterwards to redness, till the excess of sulphuric acid is expelled. The boron is then completely driven off as fluoride, and the bases remain in the form of sulphates. If only one base is present, its quantity is easily calculated from the weight of the residue. If two bases are present, *e.g.* potash and soda, the amount of sulphuric acid in the residue must be ascertained; the quantities of the two bases may then be found by the method given under INDIRECT ANALYSIS (p. 224). If more than two bases are present, they must be separated by the usual methods. The weight of the bases deducted from that of the original substance, gives the amount of boric anhydride.

Instead of driving off the boron as fluoride, it may be volatilised as borate of ethyl, by treating the pulverised borate with strong sulphuric acid and alcohol. Or the boric acid set free by the action of sulphuric acid, may be dissolved out by alcohol and separated by filtration; but this last method is applicable only when the resulting sulphates are completely insoluble in alcohol.

Boric acid combined with potash or with soda, may be estimated volumetrically by means of a standard solution of sulphuric acid. The solution is coloured with tincture of litmus, and the sulphuric acid is cautiously added from a burette, till the wine-red colour first produced by the liberation of the boric acid, changes to the bright red which indicates the presence of free sulphuric acid: this takes place as soon as the quantity of sulphuric acid (H^2SO^4) amounts to 1 at. for 2 at. of potash or soda (KHO or NaHO). Hence the amount of the base is found, and this deducted from the total weight of the dry salt, gives the boric acid.

Separation of Boron from other Elements.—When boric acid is in combination with several bases, it is best to estimate the amount of these bases at once, and determine the boric acid (or anhydride) by difference. From the metals of the first group, *copper*, for example, boron is easily separated by sulphuretted hydrogen; from *iron*, and others of the second group, by sulphide of ammonium. From *barium* it is separated by sulphuric acid; from *strontium* and *calcium*, by sulphuric acid and alcohol; from *magnesium*, by ammonia and phosphate of sodium: the precipitate in this last case generally contains a small quantity of boric acid.

The separation of boric acid from all these bases may likewise be effected by fusion with alkaline carbonates; in the case of magnesia, carbonate of potassium must be used, because soda forms with magnesia an insoluble compound.

Sulphuric acid is easily separated from boric acid by precipitation with chloride of barium; *hydrochloric, hydrobromic,* and *hydriodic* acids, by adding nitrate of silver to the solution acidulated with nitric acid; *phosphoric acid*, by ammonia and sulphate of magnesium.

The estimation of boron in presence of *fluorine* is difficult. Metallic borofluorides are analysed by heating them with sulphuric acid, whereby fluoride of boron and hydrofluoric acid are driven off, and the metal remains as sulphate, from the weight of which its quantity may be determined, and hence the amount of the boron and fluorine together. If the compound contains water of crystallisation, it must be determined by mixing the compound with 6 pts. of oxide of lead, covering the mixture in a retort with a layer of oxide of lead, and exposing it to a heat short of redness. The loss of weight gives the water.

In a mixture of a borate with a fluoride, it is impossible to determine either the boron or the fluorine exactly. By dissolving the compound in excess of nitric acid, and adding excess of carbonate of calcium, the fluorine is precipitated as fluoride of calcium, but not completely, probably because a borofluoride is formed.

The estimation of boron in *silicates* is likewise difficult. If the silicate is decomposed by acids, like datolite or botryolite, it is finely pulverised, heated in a corked flask with hydrochloric acid, at last nearly to boiling; the thick jelly is then diluted with water and filtered; the filtrate supersaturated with ammonia, which separates alumina; oxalic acid is added to precipitate lime; and the filtrate, which now contains nothing but boric acid in combination with ammonia, is evaporated in a platinum capsule over the water-bath, with frequent addition of ammonia. The dry residue is then gradually heated to redness in a covered platinum crucible, whereupon boric anhydride remains mixed with a little silica. The boric anhydride is afterwards dissolved out by water, and the residual silica weighed. The result is not quite exact, as a little boric acid goes off even in presence of excess of ammonia, but the loss is not considerable.

In silicates not decomposible by acids, boron is estimated by heating the pulverised mineral, first with hydrofluoric and then with sulphuric acid, whereby the boron and silicium are expelled as fluorides. The bases then remain as sulphates, and are determined by the ordinary methods. In another portion of the mineral, the silica is determined by fusion with a mixture of the carbonates of potassium and sodium, treatment of the residue with hydrochloric acid, evaporation to dryness, digestion of the residue in acidulated water, filtration, and washing,—whereupon the silica remains on the filter in a state of purity, and may be ignited and weighed. The bases and the silica having been thus determined, the boric anhydride is found by difference, the result being of course affected by all the errors in the several determinations. (H. Rose, Analyt. Chem. ii. 734.)

The estimation of boron in *organic compounds*, is generally effected by mixing the compound with ammonia in a capacious platinum crucible, then evaporating and igniting the residue. This method, according to Ebelmen, always involves a loss of at least 2 per cent. of boron, and that loss may even amount to 4 per cent. A better method might perhaps be to heat the compound with nitric acid in a sealed tube, according to Carius's method (p. 247): the boron would thereby be converted into boric acid, and might then be estimated by any of the methods above given.

Atomic Weight of Boron.—The earlier experiments of Gay-Lussac and Thénard, Davy, and Berzelius, in which the atomic weight of boron was estimated by the amount of oxygen absorbed in its combustion, did not lead to concordant results. Berzelius afterwards determined its value from the amount of water in crystallised borax, which in three experiments, he found to be 47·1 per cent. Now supposing the formula of the salt to be $Na^2O.2B^2O^3 + 10H^2O$, and that the atomic weight of sodium is 23, this result makes the atomic weight of boron equal to 11. Experiments by Deville, reported by Dumas (Ann. Ch. Phys. [3] lv. 129), on the proportion of chlorine in chloride of boron, gave, on the supposition that the formula of the chloride is BCl^3, the two results $B = 11·0$ and $B = 10·6$. Similar experiments with bromide of boron BBr^3, gave $B = 11·0$. This number appears therefore to have the greatest weight of evidence in its favour. If the formula of chloride of boron were BCl^2, the atomic weight of boron would be 7·3.

BORON, FLUORIDE OF. BF^3.—Discovered by Gay-Lussac and Thénard, in 1810. It is obtained: 1. By the action of boric anhydride on fluoride of calcium at high temperatures:

$$6CaF + 7B^2O^3 = 3(Ca^2O.2B^2O^3) + 2BF^3.$$

An intimate mixture of 2 pts. fluorspar and 1 pt. vitreous boric anhydride, is introduced into a gun-barrel closed at one end, and heated to whiteness in a furnace with good draught, and the gas which escapes is received over mercury: borate of calcium then remains behind.—2. By the action of hydrofluoric acid on boric acid or anhydride, viz. by heating a mixture of 1 pt. boric anhydride (or 2 pts. fused borax), and 2 pts. fluor spar, with 12 pts. oil of vitriol, in a glass vessel:

$$6CaF + B^2O^3 + 3H^2SO^4 = 3Ca^2SO^4 + 3H^2O + 2BF^3.$$

This method is easier than the former, but the gas which it yields is not quite pure, as it contains a little fluoride of silicium, resulting from decomposition of the glass; moreover part of the fluoride of boron is converted by the water into boric and hydrofluoric acids.

Fluoride of boron is a colourless gas, of pungent suffocating odour, like that of fluoride of silicium. Specific gravity = 2·37 (Davy); 2·31 (Dumas); and by calculation:

$$\frac{11 + 3\ .\ 18·7}{2} \times 0·0693 = 2·29$$

It reddens litmus, fumes in damp air, and chars organic bodies like sulphuric acid. It does not corrode glass. It is not decomposed by a red heat, or by the electric spark.

Water absorbs about 700 times its volume of this gas, with great evolution of heat and increase of bulk, forming an oily liquid of specific gravity 1·77, which when boiled, gives off $\frac{1}{5}$ of the dissolved gas, and leaves a residue consisting of $B^2O^3.6HF$, or $2BF^3.3H^2O$, which may be distilled without alteration. Water incompletely saturated with fluoride of boron, deposits boric acid on cooling, or after standing for some time, while fluoride of boron and hydrogen $HF.BF^3$, remains in solution.

Strong *sulphuric acid* absorbs 50 times its volume of gaseous fluoride of boron, forming a viscid liquid, which deposits boric acid when mixed with water.

Potassium, *sodium*, and the *alkaline earth-metals*, heated in fluoride of boron, become covered with a blackish crust, which bursts at a red heat, the metal then burning with bright incandescence, and forming a metallic borofluoride, with separation of boron. *Iron* does not act upon the gas, even at a bright-red heat. *Quick lime* absorbs fluoride of boron readily when heated, forming a fusible mixture of fluoride and borate of calcium.

Dry *ammonia gas* forms with an equal volume of fluoride of boron, a white, opaque, solid compound, $NH^3.BF^3$, which volatilises undecomposed, and is converted by water into borofluoride and borate of ammonium. By the further action of ammonia on this body, two liquid compounds, $2NH^3.BF^3$, and $3NH^3.BF^3$, are formed; when exposed to the air or heated, they give off ammonia and reproduce the solid compound.

According to Kuhlmann, fluoride of boron unites with nitric oxide, nitrous acid, peroxide of nitrogen, and nitric acid.

Fluoboric Acid. $HBO^2.3HF$.—This compound, discovered by Gay-Lussac and Thénard, is obtained by saturating water with gaseous fluoride of boron, the vessel being cooled with ice, and the gas-delivery-tube made to dip under mercury below the water, as otherwise the rapid absorption would cause the liquid to run back into the generating vessel. The saturated solution has a specific gravity of 1·77, and is nearly pure fluoboric anhydride, $B^2O^3.6HF$, or hydrate of boric fluoride, $2BF^3.3H^2O$ (Gmelin's tri-hydrofluate of boric acid, $BO^3.3HF$, Handbook, ii. 363). On heating it, one-fifth of the absorbed fluoride of boron goes off, and there remains a liquid of specific gravity 1·584, which is fluoboric acid, $H^2O.B^2O^3.6HF$, or $HBO^2.3HF$.

An easier mode of preparing this acid is to dissolve boric acid or anhydride in hydrofluoric acid contained in a platinum crucible externally cooled, avoiding an excess of boric acid, then evaporate over the water-bath, gently boil the remaining liquid in the covered crucible, till the vapours form a thick fume in the air, and leave the liquid to cool over sulphuric acid. It may also be obtained by fusing an intimate mixture of 10 pts. fluorspar and 8½ crystallised borax, pulverising the fused mass, and distilling it with 16⅔ pts. strong sulphuric acid. The product thus obtained generally contains a little silica derived from the distillation-vessel.

Fluoboric acid is an oily liquid, like oil of vitriol, fumes in the air, boils at a temperature above 100° C., and distils without alteration. It is highly caustic, chars organic bodies, and converts alcohol into ether. By dilution with water, it is decomposed, one-fourth of the boric acid being separated, and a solution of hydrofluoboric acid remaining:

$$4(HBO^2.3HF) - HBO^2 = 3HBF^4 + 6H^2O.$$

Fluoboric acid forms salts, having the general formula $MBO^2.3MF$. They are produced by the direct action of the acid on the bases, or by dissolving the corresponding borates and fluorides in the proper proportions, and leaving the solution to evaporate. But few of them have been examined.

The *sodium-salt*, $NaBO^2.3NaF + \frac{1}{2}$ aq, crystallises in small rectangular prisms, having their terminal faces obliquely truncated; they have an alkaline reaction, give off their water at 40° C., and melt at a higher temperature. The fused salt, if quickly cooled, solidifies to a clear glass; but by slow cooling, it becomes turbid, from separation of fluoride of sodium, which remains undissolved on treating the mass with cold water, whereas boiling water dissolves the whole, reproducing the original salt.

Another *fluoborate of sodium*, $NaHB^2O^4.6NaF + 10$ aq, is produced by slowly evaporating a solution of 1 at. borax and 6 at. fluoride of sodium. It crystallises in small rectangular four-sided prisms, which become turbid at 40° C. from loss of water, and behave like the preceding when melted and slowly cooled. (Handw. d. Chem. 2^{te} Aufl. ii. [2] 279.)

Hydrofluoboric Acid. $HBF^4 = BF^3.HF$.—Obtained by passing gaseous fluoride of boron into water, till the liquid is strongly acid, and exposing it to a low temperature. Boric acid then separates, and hydrofluoboric acid remains in solution:

$$4BF^3 + 2H^2O = 3BHF^4 + HBO^2.$$

A similar solution is obtained by dissolving crystallised boric acid to saturation in moderately strong hydrofluoric acid artificially cooled.

Hydrofluoboric acid is known only in the state of dilute solution. It is decomposed by concentration, yielding hydrofluoric and fluoboric acids:

$$BHF^4 + 2H^2O = HF + HBO^2.3HF.$$

In the dilute state, it does not attack glass; but if it be concentrated in a glass vessel, the glass becomes corroded, from separation of hydrofluoric acid; if, however, boric acid be added during the concentration, so as to form fluoboric acid, no corrosion of the glass takes place.

Borofluorides.—These salts, whose composition is expressed by the general formula, MBF^4 or $MF.BF^3$, are formed by the action of gaseous fluoride of boron or aqueous fluoboric acid on metallic fluorides; by the action of metallic oxides on hydrofluoboric acid; or by dissolving a metallic fluoride, together with boric acid, in aqueous hydrofluoric acid; sometimes also by merely bringing a fluoride in contact with boric acid, the liquid then becoming alkaline if previously neutral, or even if acid.

Most borofluorides are soluble in water, and are obtained in the crystalline state by evaporating their aqueous solutions. At a red heat, they are resolved into fluoride of boron and metallic fluoride. Distilled with sulphuric acid, they give off gaseous fluoride of boron and aqueous hydrofluoboric acid. They are for the most part not decomposed by heating with alkalis or alkaline carbonates.

Borofluoride of Aluminium, crystallises by slow evaporation from a solution of hydrate of aluminium in excess of hydrofluoboric acid; the crystals dissolve in water only when free acid is present. On mixing a solution of chloride of aluminium with borofluoride of sodium, a basic borofluoride of aluminium is precipitated, which, at a red heat, is resolved into fluoboric acid and borate of aluminium.

Borofluoride of Ammonium, $NH^4F.BF^3$, is obtained by subliming a mixture of the potassium-salt with sal-ammoniac, or more easily by dissolving boric acid in aqueous fluoride of ammonium, ammonia being then evolved:

$$4NH^4F + H^3BO^3 = NH^4F.BF^3 + 3H^2O + 3NH^3.$$

It crystallises by evaporation in six-sided prisms with dihedral summits; dissolves readily in water, somewhat less in alcohol; reddens litmus; does not attack glass; dissolves in aqueous ammonia, and crystallises out unaltered; sublimes when heated.

Borofluoride of Barium, $2BaBF^4.H^2O$.—Prepared by saturating hydrofluoboric acid with carbonate of barium, avoiding an excess, otherwise fluoride of barium and boric acid are produced. Crystallises from a warm solution in long needles; by slow evaporation in a warm atmosphere, in smooth rectangular prisms, often arranged in steps like common salt. Has an acid reaction; tastes like barium-salts in general; dissolves readily in water; deliquesces in moist air. Alcohol decomposes it, dissolving an acid salt, and separating a white powder. The crystals effloresce at 40° C. and decompose at a higher temperature.

Borofluoride of Calcium.—A solution of carbonate of calcium in hydrofluoric acid, deposits on evaporation, a gelatinous mass, which dries up to a white powder, reddens litmus, and is decomposed by water, with separation of a basic salt.

Borofluoride of Copper, $CuBF^4$.—Light blue needles obtained by decomposing the barium-salt with sulphate of copper, and evaporating the filtrate.

Borofluoride of Lead, $PbBF^4$.—Prepared like the barium-salt, and crystallises with difficulty by spontaneous evaporation, in four-sided prisms; from the solution evaporated to a syrup, in long prisms. Has a sweetish taste, with sour astringent aftertaste. Partially dissolved by water and by alcohol. Heated with oxide of lead, it is said to yield an easily fusible oxyborofluoride, whose aqueous solution is rendered turbid by the carbonic acid in the air.

Borofluoride of Lithium, $LiBF^4$.—Prepared like the copper-salt, and separates by evaporation at 40° C. in large prismatic crystals, which have a rather bitter and acid taste, and deliquesce in the air, sparingly soluble rhombohedral crystals then separating, which have not been further examined.

Borofluoride of Magnesium. — Easily soluble; crystallises in large prisms; tastes bitter.

Borofluoride of Potassium KBF^4. — Formed like the ammonium-salt, by adding boric acid to aqueous fluoride of potassium. It may be prepared by dissolving 2 at. (124 pts.), of crystallised boric acid, and 1 at. (138 pts.) carbonate of potassium in excess of hydrofluoric acid, or by adding a soluble potassium-salt to hydrofluoric acid; it then separates as a transparent gelatinous precipitate, which appears iridescent by reflected light while suspended in the liquid, and dries up to a white powder. It dissolves in 70 pts. of cold, and in a smaller quantity of hot water, and crystallises from the solution in anhydrous, shining, six-sided prisms. It has a bitterish taste, and does not redden litmus. Alkalis do not dissolve it more readily than pure water. Ammonia does not alter it, unless the solution contains silica, in which case a precipitate is formed. It dissolves in boiling alcohol. When heated, it first melts, then gives off fluoride of boron, and if not quite dry, likewise fluoboric acid; and after prolonged exposure to a strong heat, leaves fluoride of potassium. Strong sulphuric acid decomposes it but slowly, even with the aid of heat.

Borofluoride of Sodium, $NaBF^4$, forms short four-sided rectangular prisms, very soluble in water, less in alcohol; has a rather bitter and acid taste, and reddens litmus. The crystals are anhydrous, melt below a red heat, but require strong and prolonged ignition to decompose them completely into fluoride of boron and fluoride of sodium.

Borofluoride of Yittrum dissolves only in water containing free acid. It is obtained in crystals by dissolving yttria in excess of hydrofluoboric acid, and evaporating.

Borofluoride of Zinc, $ZnBF^4$.—Zinc dissolves in hydrofluoboric acid with evolution of hydrogen. The solution evaporated to a syrup, solidifies at low temperatures to a deliquescent mass.

BORON, IODIDE OF. Not yet obtained in the pure state. Iodine and boron strongly heated together, form a product which appears to be an oxyiodide (Wöhler and Deville). Boron does not decompose iodide of silver, even at temperatures above the melting point of the metal.

According to Inglis, a mixture of boric anhydride and charcoal heated in iodine-vapour, yields a yellow sublimate, which has not been examined.

BORON, NITRIDE OF. BN. — This compound was discovered by Balmain (Phil. Mag. [3] xxi. 170: xxii. 467; xxiii. 71; xxiv. 191), who at first regarded it as capable of uniting with metals and forming compounds analogous to the cyanides; but afterwards found that all these supposed metallic compounds were one and the same substance, viz. nitride of boron without any appreciable amount of metal. This conclusion has been confirmed by Marignac (Ann. Ch. Pharm. lxxix. 247). Balmain obtained this substance by heating boric anhydride with cyanide of potassium or cyanide of zinc, or with cyanide of mercury and sulphur. It has since been more completely investigated by Wöhler (Ann. Ch. Pharm. lxxiv. 70), who prepares it by heating to bright redness in a porcelain or platinum crucible a mixture of 2 pts. dried sal-ammoniac and 1 pt. pure anhydrous borax:

$$Na^2O.2B^2O^3 + 2NH^4Cl = 2BN + 2NaCl + B^2O^3 + 4H^2O.$$

The product is a white porous mass, which is pulverised and washed with water to free it from chloride of sodium and boric anhydride, the final washings being made with boiling water acidulated with hydrochloric acid. The boric anhydride is, however, so completely incorporated with the nitride of boron, that it cannot be wholly removed by washing. A purer product might perhaps be obtained by using neutral borate of sodium instead of borax, in which case, no excess of boric anhydride would be present:

$$Na^2O.B^2O^3 + 2NH^4Cl = 2BN + 2NaCl + 4H^2O.$$

Wöhler formerly prepared nitride of boron by igniting anhydrous borax with ferrocyanide of potassium. It is likewise produced when amorphous boron is heated to whiteness in a stream of pure nitrogen; more easily, but with simultaneous formation of boric anhydride, when boron is ignited in a current of air, or of nitrous or nitric oxide gas; also, with incandescence and evolution of hydrogen, when boron is heated in gaseous ammonia. (Wöhler and Deville, Ann. Ch. Pharm. cv. 69.)

Nitride of boron is a white amorphous powder, tasteless, inodorous, soft to the touch, insoluble in water, infusible, and non-volatile. If very pure, it exhibits when heated at the edge of a flame, a brilliant greenish-white phosphorescence, undergoing at the same time a slow oxidation. Heated in an alcohol-flame fed with oxygen gas, it burns rapidly, with faint greenish-white flame, giving off fumes of boric anhydride. It easily reduces the oxides of copper and lead, giving off nitrous fumes. Heated in a current of aqueous vapour, it yields ammonia and boric anhydride:

$$2BN + 3H^2O = B^2O^3 + 2NH^3.$$

Alkalis, and the greater number of acids, even in the state of concentrated solution, have no action on nitride of boron; strong sulphuric acid, however, with the aid of heat, ultimately converts it into ammonia and boric acid. Fuming hydrofluoric acid converts it into borofluoride of ammonium. Nitride of boron undergoes no alteration when heated in a current of chlorine. When fused with hydrate of potassium, it gives off a large quantity of ammonia. With anhydrous carbonate of potassium, it yields borate and cyanate of potassium:

$$BN + 2(K^2CO^3) = KBO^2 + KCNO.$$

It does not decompose carbonic anhydride, even at the highest temperatures.

BORON, OXIDE OF. *Boric Oxide* or *Anhydride. Anhydrous boric acid*, B^2O^3. —This the only known oxide of boron. It is formed when boron burns in oxygen gas, in the air, or in nitric oxide gas (p. 626); but it is more easily obtained by exposing boric acid, which is its hydrate, to a strong heat. Water then goes off, and the anhydride melts to a viscid mass, which, on cooling, solidifies to a colourless brittle glass (*vitrified boric* or *boracic acid*) of specific gravity 1·83. It cracks spontaneously in cooling, and the formation of each crack is attended with a flash of light (Dumas). It is perfectly fixed in the fire when alone, but in presence of water, and still more of alcohol, it volatilises to a considerable amount. It is perfectly inodorous; has a slightly bitter but not sour taste; dissolves readily in water, forming boric acid, also in alcohol. The alcoholic solution burns with a green flame; so likewise does a mixture of boric anhydride and sulphur.

Potassium heated with boric anhydride decomposes it with visible combustion; sodium decomposes it quietly. It is not decomposed by phosphorus-vapour at a red heat, or by charcoal even at a white heat (Gmelin). It unites with metallic oxides when fused with them, forming borates. From its fixity in the fire, it is capable of decomposing at high temperatures, not only carbonates, but likewise nitrates, sulphates, and indeed the salts of all acids which are more volatile than itself.

Boric Acid.

Oxide of Boron and Hydrogen. Boracic Acid. Sel sedativum Hombergii. Sel narcoticum vitrioli. H^3BO^3 or $3H^2O.B^2O^3$.—This acid is formed by the oxidation of boron in presence of water, *e. g.* by the action of nitric acid or aqua-regia on boron; also by dissolving the anhydride in water. It occurs native in the free state in many volcanic districts, especially in Tuscany, where it issues from the earth together with vapour of water, and is found, either as an efflorescence in the neighbourhood of hot springs, or dissolved in the water of small lakes or lagoons (*Laguni*), formed by the vapours themselves. It is also found in small quantity in several mineral waters, viz. in the boiling spring of Wiesbaden; in the iodine-water of Krankenheil near Fölz, and of the Kaiser spring in Aachen; in the mother-liquor of the salt-spring at Bex (Baup), and in several hepatic waters. A few borates are also found in nature (p. 626), especially borax, the acid borate of sodium, which exists in the water of certain lakes in Central Asia.

Preparation.—On the small scale, boric acid is prepared from borax. 3 pts. of crystallised borax are dissolved in 12 pts. of boiling water, and to the filtered solution is added 1 pt. of strong sulphuric acid, or so much hydrochloric acid that the liquid strongly reddens litmus. The greater part of the boric acid then separates on cooling in crystalline scales, and a larger quantity may be obtained by evaporating the mother-liquor. The crystals retain a certain portion of sulphuric or hydrochloric acid; from the latter they are easily freed by gentle heating and recrystallisation. To obtain them free from sulphuric acid, they must be fused in a platinum crucible, and then recrystallised.

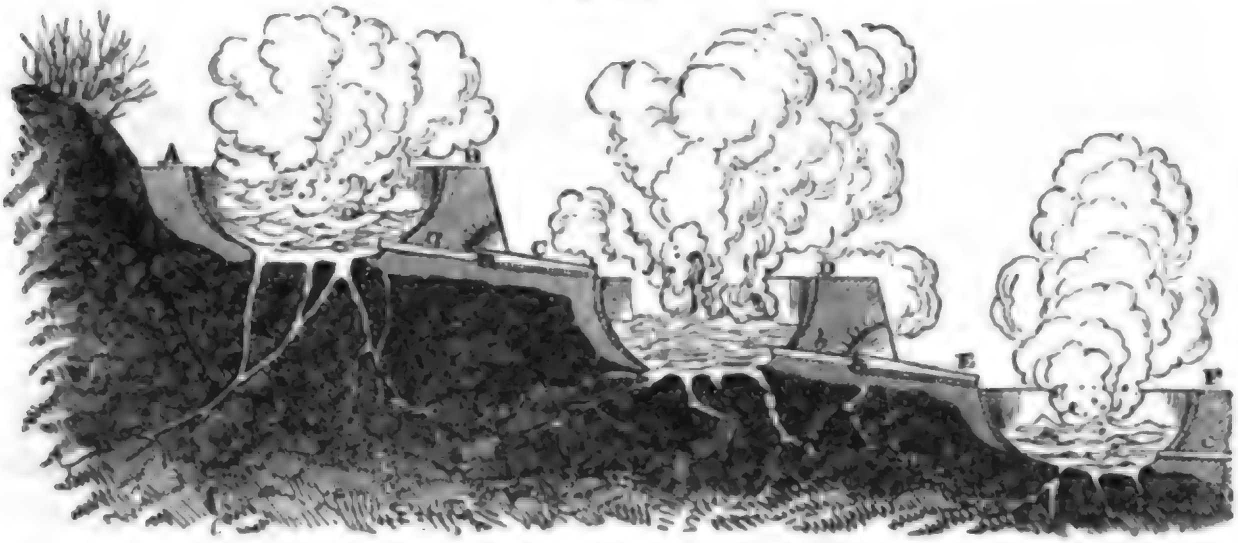
Formerly all the boric acid of commerce was obtained from borax. It was first separated in 1702 by Homberg, who prepared it by heating borax with calcined ferrous sulphate in closed vessels, whereby sodio-ferric sulphate was formed, and boric acid was carried over with the watery vapour which escaped. Boric acid may also be prepared by the decomposition of other native borates, *e. g.* borate of magnesium (*boracite*), and borate of calcium and sodium (*boronatrocalcite*).

Preparation on the large scale (Payen, Précis de Chimie industrielle, 4^{me} éd. 1859, i. 423).—All the boric acid of commerce is now obtained from the volcanic district of Tuscany, where it is discharged from the interior of the earth by numerous jets of vapour called *suffioni*, often rising in thick columns to a considerable height. The entire surface of the district, consisting of chalk and marl, is subject to constant shocks caused by subterranean agencies; and columns of boiling water are frequently projected into the air, which is also strongly impregnated with sulphuretted hydrogen. These vapours contain, besides aqueous vapour, carbonic acid, sulphydric acid, nitrogen, hydrogen, a gaseous hydrocarbon, and sometimes oxygen, together with a small quantity of boric acid and much solid matter carried up mechanically. Ch. Deville and F. Leblanc found, in the vapour of one of the suffioni, about 91 per cent. CO^2, 4 per cent. H^2S, and 5 per cent. nitrogen and combustible gases.

The vapours which issue from the clefts do not contain any appreciable quantity of boric acid, but where pools are formed round the suffioni, either artificially or by natural condensation of the vapours, the water soon becomes charged with boric acid. Probably the greater part of the acid is first deposited on the sides of the clefts before it reaches the surface, and when water penetrates into them, the acid is dissolved and thrown up in the state of solution.

To obtain the boric acid, the suffioni are surrounded with basins of coarse masonry, glazed on the inside, and large enough to enclose two or three suffioni. A series of these basins are constructed on the hill-side, and into the uppermost A B (*fig.* 106), the water of a spring is turned, and after remaining there 24 hours, during which time it is kept in a state of constant agitation by the subterranean vapour, it is made to pass through the tube *a*, into a second basin C D, where it likewise remains 24 hours, and takes up a second quantity of boric acid; thence it passes successively by the pipes *b*, *c*, into the third and fourth basins, the liquid discharged from a lower basin being continually supplied from the one above it. When the liquid has thus traversed six or eight of these lagoons, it is found to have taken up about 0·5 per cent. of boric acid, and to have a specific gravity of 1·007 to 1·010.

Fig. 106.



From the last lagoon G, H (*figs.* 107, 108), the solution passes into a large vessel I, called a *vasco*, where it deposits a quantity of mud, and afterwards into two smaller reservoirs J, K, for further clarification. From K it passes into a series of leaden pans, shown in section in *fig.* 106 and in plan in *fig.* 107, placed one above the other in the manner of terraces on a wooden scaffold. Formerly these pans were heated by wood fires; but this was found too costly, the district being nearly bare of wood; the evaporation is now performed by means of the subterranean heat, one or more of the jets of steam enclosed in pipes being conducted between the foundation and the bottom of the pans. The steam enters beneath the bottom pans, and is carried regularly upwards, so that the lowest pans, which contain the most concentrated liquid, become most heated. This mode of utilising the subterranean heat was introduced in 1817, by Count Larderel, at that time the proprietor of all the lagoons, and had the effect of converting an unprofitable branch of industry into one which is now the source of immense wealth.

Fig. 107.

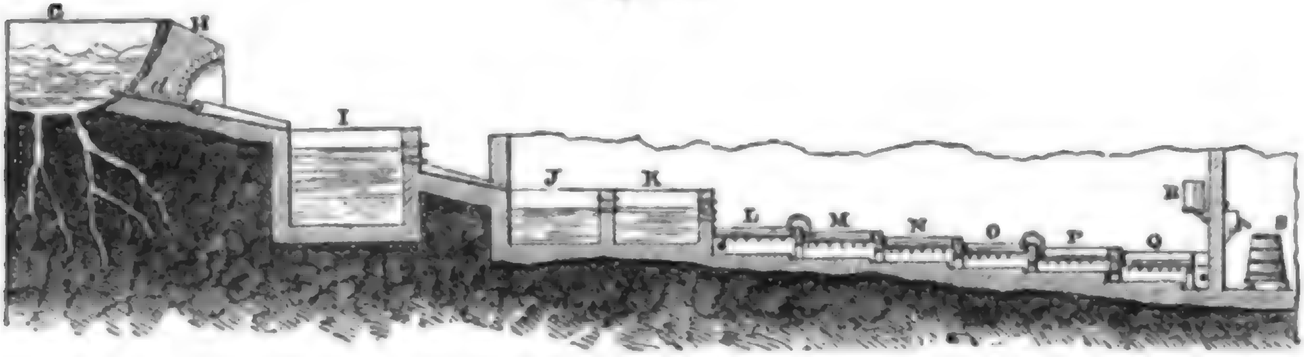
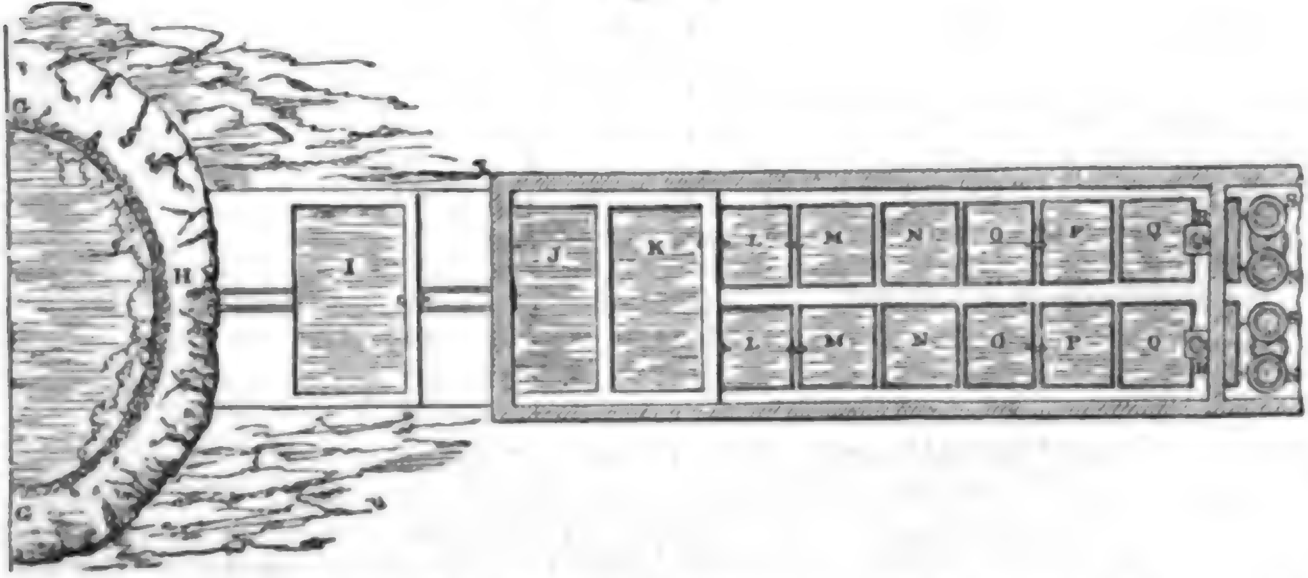
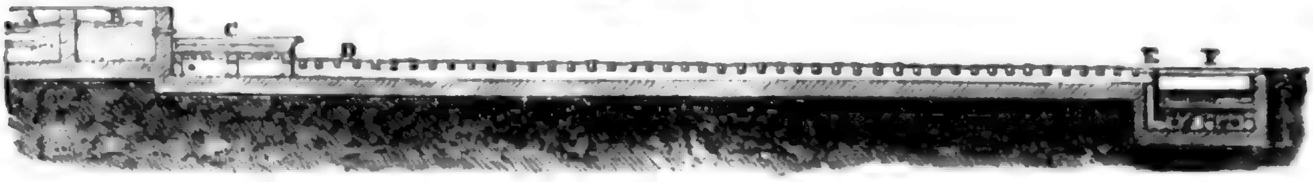


Fig. 108.



Another form of apparatus for the evaporation is shown in *fig.* 109. The liquid, after leaving the vascos A, B, passes into a shallow boiler C, from which it is made to run slowly over an inclined sheet of lead, D, E, about 150 feet long, and having corrugations on its surface, which form a series of channels. The liquid, in running over this surface, gradually evaporates, and the solution ultimately reaches the basin F, at a degree of concentration fit for crystallisation. Heat is supplied by the vapour of one of the suffioni introduced under the basin F, and carried up under the sheet of lead to C. This method of evaporation is easier than the preceding, and does not introduce so much lead into the solution.

Fig. 109.



The solution of boric acid concentrated by either of these methods, is next mixed with the mother-liquor of a preceding operation, and poured through the funnels R, into the round crystallising tubs S, S, (*figs.* 107 108, 110) which are made of wood lined with lead. The crystals are taken out after a while, and placed to drain in baskets, J, on the top of the tubs, the mother-liquor running into receivers placed under the floor.

Fig. 110.

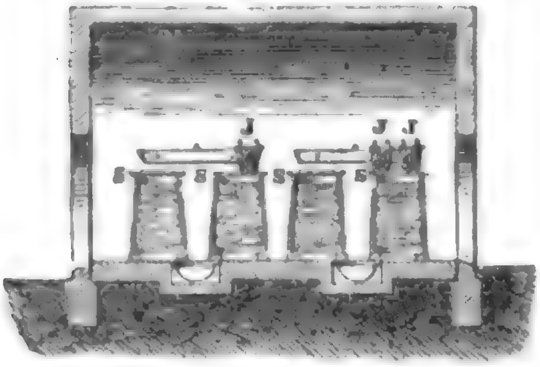
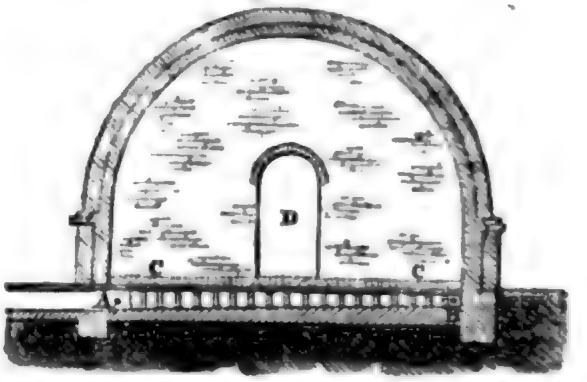


Fig. 111.



Lastly, the crystals, while still moist, are spread out on the floor C C, of the drying chamber D (*fig.* 111). This chamber has a double floor, and is heated by steam entering at A, and circulating between the two floors.

The product thus obtained is far from pure, not containing more than about 76 per cent. of boric acid. The composition of the crude acid, according to the analyses of Wittstein and Payen, is as follows:

	Wittstein.	Payen.
Crystallised boric acid	76·5	74 to 84°
Ferric sulphate	0·4	
Sulphate of aluminium	0·3	
Sulphate of calcium	1·0	2·4 to 1·2 *
Sulphate of magnesium	2·6	14·0 to 8
Sulphate of ammonium	8·5	
Sulphate of sodium	0·9	
Sulphate of potassium	0·4	
Sulphate of manganese	trace	
Chloride of ammonium	0·2	2·6 to 1·0
Silica	1·2	
Sulphuric acid	1·3	
Water	6·6	7·0 to 5·8 †

Schmidt found, in crude boric acid from Tuscany, 80 per cent. boric acid and 20 per cent. impurities, chiefly the sulphates of ammonium and magnesium. Richardson and Browell found in some samples, not more than 36 to 42 per cent. of the pure acid [? crystallised or anhydrous]. The experience of the French manufacturers of borax, seems to show that the impurities in boric acid from Tuscany become greater year by year, which may perhaps be due to the increasing disintegration of the earthy strata by the aqueous and acid vapours.

Of the origin of the vapours by which the boric acid is brought to the surface, nothing certain is known. Dumas has suggested that they may proceed from a deep-seated bed of sulphide of boron, with which the water of lakes, or of the sea, comes in contact, thereby producing boric and sulphydric acids. Part of the boric acid may thus be supposed to act upon the carbonates of calcium and magnesium in the soil, converting

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* Including sand, clay, &c.

† Including organic matter.

them into borates, and setting free carbonic anhydride. The sulphuretted hydrogen being oxidised by the air, yields free sulphur, which is deposited on the edges of the suffioni. The ammonia and organic matter are derived from the water, and the saline impurities from the water and the earthy strata, through which the vapours make their way. Bolley supposes that the boric acid and ammonia may result from the action of solution of sal-ammoniac at a boiling-heat, on borates contained in the earth; and according to Warington, the formation of these products may be ascribed to the action of water on nitride of boron. There is, however, nothing positive to indicate the nature of the particular compound or compounds of boron, to which the elimination of the boric acid is really due.

Properties.—Boric acid crystallises from water in white, translucent, nacreous, six-sided laminæ, somewhat unctuous to the touch; it is inodorous, and has a faint, scarcely acid, rather bitterish, cooling taste. Specific gravity = 1·48. It dissolves in 2·57 parts of water at 18° C.; in 14·9 parts at 25°, in 10·7 parts at 50°, in 4·7 parts at 75°, and in 2·97 parts at 100°. (Brandes and Firnhaber.) It is still more soluble in alcohol and in volatile oils.

Boric acid dissolves in warm concentrated sulphuric, nitric, or hydrochloric acid, but separates for the most part on cooling, or on addition of water. Its solubility in water is increased by addition of tartaric acid, tartrate of potassium, Rochelle salt, racemic acid, or alkaline racemates.

The crystallised acid heated to 80°—100° C., gives off 21·8 per cent. water, that is to say, half the quantity which it contains, leaving $H^6B^4O^9$ or $3H^2O.2B^2O^3$ (according to Schaffgotsch, it gives off nearly all its water at 100° C.); by prolonged heating to 160° it is deprived of 2 at. water more, leaving $H^2B^4O^7 = H^2O.2B^2O^3$, and at a stronger heat, the remaining water goes off, leaving the anhydride B^2O^3, as a fused viscid mass, which solidifies to a fissured glass on cooling (p. 635).

Reactions.—A cold saturated aqueous solution of boric acid colours litmus-tincture wine-red (the tint of port wine), like carbonic acid, but a hot saturated solution colours it bright red. Turmeric paper moistened with the alcoholic solution of boric acid acquires a reddish-brown colour, quite different from that produced by alkalis, and becoming distinct only after drying: it is intensified by acids, especially by hydrochloric, sulphuric, nitric, and tartaric acids, and turned black by alkalis.

The alcoholic solution of boric acid burns with a beautiful green-edged flame, a reaction which is quite characteristic of boron, provided copper and certain chlorine-compounds are absent. This green colour is not produced, however, when the acid is in combination with an alkali or other base; and its production is partly prevented by the presence of chloride of sodium or calcium, and even by small quantities of tartrate of potassium or Rochelle salt (doubtless because these salts are partly decomposed by the boric acid, and neutralise it), also by free tartaric acid or phosphoric acid. In either of these cases, the green colour appears on addition of sulphuric acid, or of a considerable quantity of hydrochloric acid (H. Rose, Pogg. Ann. cii. 545). It must be observed, however, that a green flame, though of a more bluish tint, is produced when hydrochloric acid itself is dropped into burning alcohol. (See p. 630.)

For the reactions with metallic salts see p. 640.

Borates. (Berzelius, Traité, vol. i—iv. Gm. vol. i—vi. Handw. d. Chem. 2te Aufl. ii. [2] 303. H. Rose, Pogg. Ann. ix. 76; lxxxvi. 581; lxxxvii. 1, 470 and 587; lxxxviii. 299, 482; xci. 452. Wöhler, *ibid.* xxviii. 525. Rammelsberg, *ibid.* lxix. 445. Ebelmen, Ann Ch. Phys. [3] xxxiii. 34. Herapath, Ann. Ch. Pharm. lxxii. 254. Bolley, *ibid.* lxviii. 122. Laurent, Ann. Ch. Phys. [2] lxvii. 215. Tissier, Compt. rend. xxxix. 192; xlv. 411. Bloxam, Chem. Soc. Qu. J. xii. 177; xiv. 143.)—Boric acid forms salts in which the proportion of anhydrous base (M^2O) to anhydrous acid (B^2O^3), or of metal to boron, ranges between the limits 9 : 1 and 1 : 6. Those which contain equal proportions of base and acid are usually regarded as neutral or normal borates, the rest as basic or acid. The following proportions have been observed:

Basic.	Neutral.	Acid.
$9M^2O.B^2O^3$	$M^2O.B^2O^3$	$2M^2O.3B^2O^3$
$6M^2O.B^2O^3$		$M^2O.2B^2O^3$
$9M^2O.2B^2O^3$		$M^2O.3B^2O^3$
$3M^2O.B^2O^3$		$M^2O.4B^2O^3$
$5M^2O.2B^2O^3$		$M^2O.5B^2O^3$
$2M^2O.B^2O^3$		$M^2O.6B^2O^3$
$3M^2O.2B^2O^3$		

Most of the so-called acid borates, however, contain several atoms of water; and if the whole or part of this water be regarded as basic, we shall find that nearly all borates may be arranged in two classes, orthoborates and metaborates (so called from their analogy with the ortho- and meta-phosphates and silicates), the composition of which may be represented by the following general formulæ, the symbol M denoting either a single metal, or two, or three metals, including hydrogen:

$$\text{Orthoborates } 3M^2O.B^2O^3, \text{ or } M^3BO^3 = \left.\begin{matrix} M^3 \\ B''' \end{matrix}\right\} O^3$$

$$\text{Metaborates } n(M^2O.B^2O^3), \text{ or } M^nB^nO^{2n} = \left.\begin{matrix} M^n \\ (B''')^n \end{matrix}\right\} O^{2n}$$

The latter formula, which, when $n = 1$, becomes that of the so-called neutral borates, MBO^2, includes the greater number of the salts of boric acid. Nevertheless it appears probable that boric acid is essentially tribasic, and that the borates containing 3 at. metal to 1 at. boron are its normal salts (hence called orthoborates): for crystallised boric acid contains H^3BO^3; and there are boric ethers containing 3 at. alcohol-radicle to 1 at. boron, whereas none are known of the form RBO^2. Moreover it appears from the experiments of Bloxam, that boric acid, when ignited with metallic hydrates, mostly drives out 3 at. of water, forming a trimetallic borate, except in the case of hydrate of potassium, in which the water is retained with peculiar force; and when heated to bright redness with carbonates, it expels a quantity of carbonic anhydride approaching more nearly to 3 atoms as the base is weaker, that limit being actually reached in the case of strontia. (See BORATES OF BARIUM, LITHIUM, POTASSIUM and SODIUM.) There appear also to be a few borates intermediate in composition between ortho- and metaborates, viz. $M^4B^2O^5 = M^3BO^3.MBO^2$.

Borates containing more than 3 at. metal to 1 at. boron may be regarded as compounds of orthoborates with metallic oxides or hydrates (see BORATES OF ALUMINUM); and those anhydrous borates which contain more than 1 at. boron to 1 at. metal may be regarded as metaborates combined with boric anhydride; *e.g.* anhydrous borax, $Na^2O.2B^2O^3 = 2NaBO^2.B^2O^3$.

Borates are formed by the action of boric acid on metallic oxides or their salts, either in the wet or in the dry way. At high temperatures, boric acid or anhydride decomposes carbonates, sulphates, chlorides, and indeed the salts of all volatile acids. Acid borates, borax for example, take up additional quantities of base when ignited with metallic oxides, and likewise decompose the salts of volatile acids. In the wet way, on the contrary, boric acid acts as a very weak acid, being separated from its combinations completely by most acids, and partially, under certain circumstances, even by carbonic acid, sulphydric acid, and water. In concentrated solution, however, it decomposes carbonates, especially at the boiling heat; also soluble sulphides and precipitated sulphide of manganese. It has but little power of neutralising the alkaline reaction of the stronger bases, so that even the solutions of many of the polyacid borates exhibit a strong alkaline reaction to litmus, which is not neutralised till the base is combined with 5 or 6 atoms of boric acid, and even then the liquid does not exhibit an acid reaction.

The borates of the alkali-metals dissolve readily in water, but are precipitated by alcohol. All other borates dissolve but sparingly soluble in water; but none are perfectly insoluble. The sparingly soluble borates may be obtained by precipitation. Many of these precipitates are soluble in excess of the soluble metallic salt from which they have been formed, but not in excess of alkaline borate; *e.g.* the precipitate formed by borax dissolves in solution of chloride of barium, but not of borax: they are often likewise soluble in chloride of ammonium and in free boric acid. The sparingly soluble borates are easily decomposed by water, especially when boiled with it, the boric acid being sometimes almost completely removed. Hence it is very difficult to obtain these salts in the pure state. H. Rose, in his elaborate investigation of the borates, purified the precipitates as completely as possible by repeated pressure between paper without washing, and afterwards estimated the quantity of foreign salts still attached to the precipitate. The soluble borates are likewise decomposed by water. If a strong solution of borax be mixed with slightly reddened tincture of litmus, the liquid retains its faint red colour, but on dilution with water becomes distinctly blue, behaving indeed like a dilute solution of free alkali mixed with boric acid. Neutral borates of alkali-metal exhibit a similar reaction.

When a solution of an alkaline borate coloured with tincture of litmus is gradually mixed with sulphuric acid, the liquid exhibits a wine-red colour till all the alkali is saturated with sulphuric acid; after that, a single drop of sulphuric acid produces the bright red colour.

Solutions of alkaline borates absorb carbonic and sulphydric acid gases; expel ammonia from its salts when boiled with them, like dilute alkalis; their dilute solutions also react like alkalis with mercury and silver-salts, and with many organic substances. (See BORAX, p. 648.)

The soluble borates, both neutral and acid, give white precipitates with solutions of chloride of barium, chloride of *calcium*, *alum*, sulphate of *zinc* and nitrate of *lead*; reddish with sulphate of *cobalt*; greenish with sulphate of *nickel*; yellowish with *ferric* sulphate in the cold, brown on boiling. These precipitates dissolve easily in sal-ammoniac; and if they have been produced by an acid borate of alkali-metal, borax for example, they dissolve pretty readily in an excess of the salt from which they have been obtained; The precipitates formed by neutral borates of alkali-metal in the same solutions exhibit similar characters, excepting that they are less soluble in excess of the earth-metal or heavy metal salt.

Solution of borax or of monoborate of sodium, does not precipitate sulphate of *magnesium* in the cold; but on heating, a precipitate forms which disappears again on cooling; completely; if formed by the acid borate; nearly, if by the neutral borate. Both neutral and acid borates of alkali-metal form with manganous salts, a precipitate insoluble in excess of the latter, easily soluble in sal-ammoniac.

Dilute solutions of neutral borates of alkali-metal form with nitrate of *silver*, a brown precipitate of nearly pure oxide of silver, insoluble in excess of water, easily soluble in ammonia or nitric acid. A concentrated solution of neutral borate forms with silver-salts, a brown precipitate which dissolves in a large quantity of water, leaving only a slight residue of oxide of silver. Concentrated solutions of acid borates of alkali-metal form with nitrate of silver a white precipitate of borate of silver, completely soluble in a large quantity of water. Borate of ammonium forms a white precipitate in concentrated silver-solutions, none in dilute solutions.

Soluble borates, whether neutral or acid, give with *mercuric chloride*, a brown precipitate of oxychloride, insoluble in excess of the mercury-salt. Concentrated solutions give with neutral *mercurous nitrate*, a yellow-brown precipitate, soluble in much water: dilute solutions, a blackish-grey precipitate which remains long suspended. Basic mercurous nitrate forms with a strong solution of borax, a dingy, yellow-brown precipitate which dissolves in a large quantity of water, leaving black mercurous oxide.

If the solution of a calcium or magnesium salt be mixed with excess of boric acid, and to the boiling solution borax be added in quantity just sufficient to neutralise the acid of the calcium or magnesium salt, no precipitate is formed; similarly with salts of manganous, ferrous, cobalt, nickel, cadmium and zinc salts; but solutions of aluminium, chromicum, ferricum, stannicum, lead and copper, yield precipitates when thus treated. (Tissier.)

For the reactions of borates with fluorspar and acid sulphate of potassium before the blowpipe (see p. 630).

Borates of Aluminium.—A solution of alum mixed with alkaline borates yields precipitates which, according to H. Rose, are double salts of borate of aluminium and borate of the alkali-metal mixed with sulphate of potassium; water abstracts the greater part of the latter and of the alkaline borate, leaving a basic borate of aluminium. In this manner, the precipitate produced by monosodic borate yields sexbasic borate of aluminium, $2(Al^4O^3)'''.B^2O^3 + 3\,aq. = 6al^2O.B^2O^3 + 3\,aq.$, which may also be regarded as an orthoborate combined with 3 at. hydrate of aluminium $= al^3BO^3.3alHO$.—By adding acid borate of sodium (borax) to solution of alum, a precipitate is formed containing $3(Al^4O^3)'''.2B^2O^3 + 7\,aq. = 9al^2O.2B^2O^3 + 7\,aq.$ or $2al^3BO^3.3alHO + 2\,aq.$

Ebelmen, by heating a mixture of alumina and borax for a long time in a porcelain furnace, obtained a nonobasic salt $3(Al^4O^3)'''.B^2O^3 = 9al^2O.B^2O^3$ or $al^3BO^3.3al^2O$.

Borates of Ammonium.—Boric acid forms with ammonia, several salts which may all be regarded as metaborates, expressed by the general formula $M^nB^nO^{2n}$, the *n* at. M being made up partly of ammonium, partly of hydrogen.

a. $(NH^4)^3HB^4O^8$ is obtained by saturating crystallised boric acid with dry ammonia gas, or by dissolving one of the following salts in warm concentrated aqueous ammonia. The salt obtained by the former process contains 4 at., that by the latter 1 at. water of crystallisation.

b. $(NH^4)HB^2O^4 + \frac{3}{2}aq.$ crystallises from a solution of boric acid in excess of ammonia, in very efflorescent crystals of the dimetric system, soluble in 12 pts. of water. It effloresces like the preceding, giving off part of its ammonia.

c. $(NH^4)H^3B^4O^8 + 2\,aq.$ is obtained, according to Arfvedson, by dissolving boric acid in warm caustic ammonia, till the alkaline reaction is nearly neutralised. The liquid, if slowly cooled, deposits rhombic crystals, exhibiting, according to Schabus, the faces $oP . P . \infty P . \infty P \infty$, and often assuming a prismatic form from the predominance of oP and of four P-faces situated in the same zone; sometimes twin crystals occur. It is permanent in the air, dissolves in 8 pts. of cold water, gives off ammonia on boiling, and leaves boric anhydride when ignited. A salt called *Larderellite*, of similar constitution, but containing less water of crystallisation, viz. $(NH^4)HB^2O^4 + \frac{1}{2}aq.$ was found by Bechi in the boric acid formations of Tuscany, in yellowish-white, transparent, tasteless crystals, exhibiting under the microscope, the form of rectangular tablets, and by polarised light the optical appearances of gypsum. It dissolves in water, but the solution when evaporated deposits the salt $(NH^4)H^5B^6O^{12} + 2aq$.

d. $(NH^4)H^4B^5O^{10} + \frac{3}{2}aq.$ (Laurent) $+ 2aq.$ (Rammelsberg). First prepared by L. Gmelin, who, however, supposed it to contain 4 at. boric acid to 1 at. ammonia (Handbook ii. 436). According to Rammelsberg, however, it has the composition above given, and is isomorphous with the corresponding potassium-salt. According to Laurent, it is obtained by dissolving excess of boric acid in aqueous ammonia and recrystallising. It forms small shining prisms of the monoclinic system, generally in cruciform groups. It is permanent in the air, dissolves in about 8 pts. of cold water, and, like the preceding salts, has an alkaline reaction. The solution gives off ammonia when boiled, and the residue solidifies to a granular crystalline mass, which is permanent in the air, and appears to contain 6 at. boric acid to 1 at. ammonia.

e. $(NH^4)^2H^3B^5O^{10} + aq.$ is obtained by dissolving boric acid in aqueous ammonia. (Arfvedson.)

A solution of borate of ammonium has been successfully used for rendering muslin and other light fabrics non-inflammable. When tissues thus impregnated are held in the flame of a candle, they are merely carbonised, the water and ammonia which escape preventing the communication of the flame. If the contact with the flame be prolonged, the boric acid melts and forms a glassy varnish round the charred tissue, which prevents it from taking fire.

Borate of Amyl. See Boric Ethers (p. 649).

Borates of Barium.—Boric acid ignited with excess of hydrate of barium expels 3 at. water, and forms the *tribarytic orthoborate*, Ba^3BO^3. Heated with excess of carbonate of barium, it expels 2 at. carbonic anhydride at a dull red heat, and $2\frac{1}{2}$ at. at a bright red heat, forming the anhydrous salts, $Ba^4B^2O^5 = 2Ba^2O.B^2O^3$ and $Ba^{10}B^4O^{11} = 5Ba^2O.2B^2O^3$. (Bloxam.)

By precipitating barium-salts with borates of the alkali-metals, borates of barium are obtained, mostly as white crystalline powders, differing in composition according to the composition and relative proportions of the salts employed, the temperature of the solutions, and the duration of the washing. They are probably all metaborates.

a. *Monometaborate*, $BaBO^2 + 5aq.$ (or possibly a monobarytic orthoborate, $BaH^2BO^3 + 4aq.$), was obtained by Berzelius by precipitating chloride of barium with monoborate of potassium. According to H. Rose, when prepared from cold solutions, and dried at 100° C. after pressure between paper, but without washing, it has the composition $BaBO^2 + \frac{1}{2}aq.$, and when precipitated from very hot solutions it contains more than $\frac{1}{2}$ aq., but less than 1 aq. To drive off all the water requires a strong heat. The salt dissolves in cold, and more readily in hot water, especially in presence of ammoniacal salts, and therefore cannot be completely washed.

b. *Sesquimetaborate.* $Ba^2HB^3O^6 + 7aq.$—Laurent obtained this salt by mixing a solution of chloride of barium with pentaborate of sodium, under circumstances not particularly specified. According to H. Rose, the precipitate obtained by mixing chloride of barium with an acid borate of alkali-metal, has, when dried at 100° C., the composition $Ba^3H^2B^5O^{10} + \frac{7}{2}aq.$

c. *Dimetaborate*, $BaHB^2O^4 + 2aq$, is precipitated in white flocks when a solution of nitrate of barium is added by drops to excess of solution of borax mixed with ammonia. It dissolves in 100 pts. of water, more easily in ammoniacal salts and in excess of chloride of barium. (Laurent.)

d. *Trimetaborate.* $BaH^2B^3O^6 + 6aq.$—Precipitated as a white crystalline powder, when a warm solution of nitrate of barium is added by drops and with stirring, to excess of pentaborate of sodium.

Borates of Cadmium.—The precipitate formed on mixing the cold solutions of borax and sulphate of cadmium contains, after being merely pressed, the *monoborate*, $CdBO^2$, mixed with a small quantity of an acid salt. The precipitate from boiling solutions consists chiefly of $2CdBO^2.CdHO + aq.$

Borates of Calcium. a. *Orthoborate.* CaH^2BO^3 (dried at 100° C.)—The formula might also be that of a monometaborate, $CaBO^2 + H^2O$, but the first view of its constitution is the more probable, inasmuch as the salt gives off 1 at. H as water, only at 200° C., and is not completely dehydrated even at 300°. It is produced by precipitating chloride of calcium with monoborate of sodium, probably also when solution of borax is precipitated by lime-water. It is somewhat soluble in water, and is decomposed by hot water.

b. *Sesquimetaborate*, $Ca^2HB^3O^6$, appears to be precipitated, together with variable quantities of the dimetaborate, when calcium-salts are mixed with solution of borax (H. Rose). A similar composition appears to belong to *rhodicite*, a mineral found in the Ural, in small, hard, shining, yellowish-white crystals of tetrahedral habit. It has not been exactly analysed, but appears to contain 4B to 3Ca. (G. Rose.)

c. *Dimetaborate*, $CaHB^2O^4$.—Obtained, according to Tünnermann, when borax is precipitated by nitrate of calcium. It occurs also as a white efflorescence composed of crystalline needles containing $\frac{5}{2}$ at. water, on the plain of Iquique in Ecuador, South America, forming the mineral called *borocalcite*, *hydroborocalcite*, or *hayesite* (Ulex). Bechi found a calcic diborate with $\frac{3}{2}$ aq. in an old lagoon-crater in Tuscany.

d. *Tetrametaborate*. $CaH^3B^4O^8 + \frac{3}{2}$ aq.—Precipitated on boiling milk of lime with excess of boric acid.

Borate of calcium occurs associated with silicate of calcium in *botryolite* and *datolite* (*q. v.*), and with magnesia in *hydroboracite* (*q. v.*)

Borate of Cobalt is probably contained in the glass fluxes formed with cobalt-compounds and borax. Cold solutions of a cobalt-salt and borax yield a reddish precipitate, which, after drying at 100° C., consists chiefly of $2CoBO^2.CoHO + \frac{3}{2}$aq. It is soluble in water, and melts to a blue glass when strongly heated.

Borates of Copper.—It is difficult to obtain these salts in a definite state. Sulphate of copper mixed with solutions of alkaline borates, yields precipitates consisting of compounds of borate and oxide of copper mixed with sulphate of soda and basic sulphate of copper, which are decomposed by water, leaving a residue composed of oxide and borate of copper, but with less boric acid than the original precipitate. Cold concentrated solutions of cupric sulphate and monoborate of sodium yield a precipitate which, after washing, consists of $CuHO.2CuBO^2$ + aq. The precipitate from the same solutions mixed hot is, after washing, $CuHO.2CuBO^2$. That obtained in like manner from cold concentrated solutions of cupric sulphate and borax is an orthoborate containing 2 at. copper, viz. $(Cu^2H)BO^3 + \frac{1}{2}$aq. The same precipitate is obtained from hot concentrated solutions of cupric sulphate and borax, especially if the copper-salt is in excess. It is a loose blue-green powder, sparingly soluble in water, but decomposed by water, leaving the compound $CuBO^2.3CuHO + \frac{1}{2}$aq. Cold *dilute* solutions of the same salts yield a precipitate containing 5Cu to 2B and 5H, while the precipitate from hot dilute solutions contains 10 or 12 at. Cu to 1 at. B.

Bolley has suggested the use of the green precipitate, obtained from cold solutions of 2 pts. cupric sulphate (blue vitriol), and 3 pts. borax, as a substitute for the arsenical greens used in painting, paper-staining, and calico-printing.

Borate of Ethyl. See **Boric Ethers** (p. 650).

Borates of Iron.—*Ferric monometaborate*, $Fe^2O^3.3B^2O^3$ + 3 aq. or $\mathit{fe}BO^2 + \frac{3}{2}$ aq. has not been prepared artificially, but has been found by Bechi in an old lagoon-crater in Tuscany: hence called *Lagunite*.

Ferric orthoborate, $Fe^4O^3.B^2O^3$ or fe^3BO^3, is not known in the separate state, but only in combination with borate of sodium or with ferric oxide. On mixing a solution of ammonioferric sulphate (ammonia-iron-alum) with monometaborate of sodium, a bulky precipitate is formed, which, after being pressed between paper, but not washed, is a sodio-ferric borate containing $NaBO^2.4\mathit{fe}^3BO^3$ + 3 aq. Cold water abstracts boric acid and borate of sodium, leaving an oxyborate, which, after drying at 100° C., is $6Fe^4O^3.B^2O^3$ + 6 aq. or $15\mathit{fe}^2O.2\mathit{fe}^3BO^3$ + 6 aq. By precipitating ammonioferric sulphate with borax, a light brown bulky precipitate is formed containing $NaH^3B^4O^8.4\mathit{fe}^3BO^3$ + aq., and reduced by washing with water to $24\mathit{fe}^2O.2\mathit{fe}^3BO^3$ + 9 aq. or $9Fe^4O^3.B^2O^3$ + 9 aq.

Borates of Lead.—*a.* The *monometaborate*, $PbBO^2 + \frac{1}{2}$ aq. is obtained, according to Herapath, when the precipitate formed by borax in a neutral lead-salt, is digested for some hours with strong ammonia. It is said also to be produced when a solution of basic acetate of lead is partially precipitated by borax, and, according to H. Rose, by washing with cold water the precipitate formed on mixing the cold solutions of borax and nitrate of lead. It is a white, amorphous, heavy powder, insoluble in water and in alcohol, soluble in dilute nitric and in warm acetic acid, from which solutions it is precipitated by ammonia. It gives off some of its water at 120° C., the whole at 160°, and at a red heat, melts to a colourless glass, of specific gravity 5·598.

b. The *sesquimetaborate*, $Pb^2HB^3O^6 + \frac{3}{2}$aq. formed by adding a large excess of borax to a boiling solution of a lead-salt, resembles the preceding, gives off 1 at. water between 170° and 200° C., and melts to a colourless glass, of specific gravity 5·235. (Herapath.)

c. Dimetaborate, $PbHB^2O^4 + \frac{3}{2}$aq. obtained by boiling the salt *b* with borax. Light amorphous powder, which gives off its water between 200° and 230° C., and at a red heat melts to a vitreous mass (Herapath). When 100 pts. lead-oxide are fused with 64 pts. boric anhydride (1 : 2 at.), a nearly colourless glass is obtained as hard as flint-glass, and possessing much higher refractive power.

Basic borates.—According to H. Rose, the precipitates formed with nitrate of lead and either mono- or di-borate of sodium, are frequently basic salts, probably mixtures of monoborate and hydrate of lead, varying in composition according to the strength of the solutions and the duration of the washing. Hot, very dilute solutions, give a precipitate to which Rose assigns the formula $3(PbO.BO^3) + PbO.HO + aq.$, or $2(3PbBO^2.PbHO) + aq.$

Borochloride of Lead, $PbBO^2.PbCl + \frac{1}{2}aq.$ is obtained by mixing hot solutions of borax and chloride of lead, and crystallises in very small, irregular, nacreous needles, which are not decomposed by cold water, but gradually by boiling water. It gives off all its water between 120° and 150° C.

Boronitrate of Lead, $PbBO^2.PbNO^3$, is deposited in irregular shining crystals, from a solution of borate of lead in nitric acid, evaporated till a film forms on the surface, At 120° C. the crystals give off water and a little nitric acid, and at a higher temperature evolve nitrous acid and melt to a colourless glass.

Borate of Lithium.—Boric acid heated to bright redness with carbonate of lithium, expels 2½ at. carbonic anhydride, forming the salt $5Li^2O.2B^2O^3$. (Bloxam.)

Borates of Magnesium. *a. Orthoborate.* Mg^3BO^3.—Ebelmen obtained this salt by fusing magnesia with boric anhydride, and exposing the vitreous mass, in a platinum dish, to the strongest heat of a porcelain furnace for several days, till the excess of boric anhydride was volatilised. It formed radiating nacreous crystals, of specific gravity 2·987. It is also obtained as a hydrate, $Mg^3BO^3 + 5aq.$ by boiling a mixture of borax and sulphate of magnesium, and washing the precipitate (which contains borate of sodium, magnesia, and hydrate of magnesium) with cold water. When boiled with water, it gives up part of its acid, and leaves a basic salt which absorbs carbonic acid from the air. The precipitate formed by boiling sulphate of magnesium with borax, redissolves completely on cooling.

b. *Monometaborate*, $MgBO^2$.—Obtained as an amorphous precipitate, containing 2 at. water, on mixing the hot solutions of borax and nitrate of magnesium (Laurent). The same salt, but with 4 at. water, was obtained, according to Wöhler, when a mixed solution of borax and sulphate of magnesium, which had been heated, and had afterwards become clear by cooling, was left to itself for several months in winter in a place where the temperature often fell below 0° C. It formed slender radiating needles, insoluble in water, soluble in dilute acids, reprecipitated in needles by ammonia, giving off water and becoming turbid when heated. *Boracite*, from Segeberg in Holstein, appears to be a monoborate of magnesium, while that from Luneburg is a mixture or compound of $3Mg^2O.4B^2O^3$, or $6MgBO^2.B^2O^3$, with MgCl.

c. *Trimetaborate*, $MgH^2B^3O^6 + 3aq.$ separates, according to Rammelsberg, in crystalline crusts, when a concentrated solution of boric acid is boiled with carbonate or hydrate of magnesium and the filtrate is evaporated.

d. *Tetrametaborate*, $MgH^3B^4O^8 + aq.$—This, according to Laurent, is the composition of the last crops of crystals deposited when a solution obtained by boiling boric acid with magnesium is left to evaporate spontaneously.

e. *Hexmetaborate*, $MgH^5B^6O^{12} + \frac{13}{3}aq.$—Granular salt obtained by heating hydrate of magnesium with excess of boric acid; melts to a porcelain-like mass (Rammelsberg). Perhaps a mixture of one of the preceding salts with free boric acid.

Magnesio-chromic Borate.—A salt containing $6Mg^2O.3Cr^4O^3.2B^2O^3$, is obtained by heating for five days in the porcelain furnace a mixture of 20 grm. chromic oxide, 15 grm. magnesia, and 20 grm. boric anhydride, being deposited in the cavities of the fused mass in grass-green microscopic crystals, of specific gravity 3·82. (Ebelmen.)

Magnesio-ferric Borate, $6Mg^2O.3Fe^4O^3.2B^2O^3$, is obtained by fusing in like manner a mixture of 25 grm. ferric oxide, 20 grm. magnesia, and 25 grm. boric anhydride, in small, black, prismatic crystals, of specific gravity 3·85.

Borate of Methyl. See Boric Ethers (p. 650).

Borate of Nickel.—Cold solutions of borax and sulphate of nickel yield a precipitate of $NiBO^2 + aq.$ or NiH^2BO^3, from which cold water abstracts boric acid, leaving a salt containing $2NiBO^2.NiHO + 2aq.$ By boiling for some time with borax, this precipitate is converted into the dimetaborate, $NiHB^2O^4$.

Borates of Potassium.—a. The *monometaborate*, KBO^2, is formed by melting together 70 pts. (1 at.) boric anhydride, and 138 pts. (1 at.) carbonate of potassium. It melts at a white heat, has a caustic alkaline taste, dissolves in water, and separates slowly from the solution in ill-defined crystals which, according to Schabus, are monoclinic. The solution should be evaporated out of contact with the air, as it absorbs carbonic acid. Boric anhydride, heated to redness with excess of hydrate of potassium, expels 2 at. carbonic anhydride, forming the salt $K^4B^2O^5 = 2K^2O.B^2O^3$. (Bloxam.)

b. The *dimetaborate*, KHB^2O^4, is prepared by supersaturating a boiling solution of carbonate of potassium with boric acid, and then adding pure potash in sufficient quantity to produce a strong alkaline reaction. It crystallises sometimes with 2aq. sometimes with 2½aq. The hydrate, $KHB^2O^4. + 2aq.$, forms regular six-sided prisms, which dissolve readily in water with strong alkaline reaction, and swell up considerably when heated. The other hydrate, $KHB^2O^4 + \frac{5}{3}aq.$: forms right rhombic prisms of 98° 35′, with basic brachydiagonal end-faces. It behaves like the former hydrate, but when kept in a closed vessel, separates into a liquid and a solid salt, apparently the hydrate with 2 aq.

c. *Trimetaborate*, $KH^2B^3O^6 + 3aq.$ or perhaps, *tri-orthoborate*, $KH^8B^3O^9$.—Obtained like the preceding, but with a smaller quantity of caustic potash. Separates in rectangular prisms, with four-sided pyramidal summits. Permanent in the air; melts without much tumefaction. (Rammelsberg.)

f. *Pentametaborate*, $KH^4B^5O^{10} + 2aq.$—Formed when a boiling solution of carbonate of potassium is mixed with a sufficient quantity of boric acid to produce a strong acid reaction. The solution on cooling deposits small shining prisms, isomorphous with the corresponding ammonium-salt. Permanent in the air, sparingly soluble in cold, easily in hot water; neutral. (Rammelsberg.)

BORATES OF SILVER.—The precipitates formed in solution of nitrate of silver by alkaline borates vary in composition according to the dilution and temperature of the the solutions. Very dilute solutions, especially if hot, yield a precipitate of pure oxide of silver (H. Rose). A moderately dilute silver-solution mixed with a strong solution of borax, yields a flocculent precipitate of the *monometaborate* $AgBO^2$, which when dry is a white powder blackened by light. It dissolves in a large quantity of water; but is decomposed by a small quantity; melts at a gentle heat. The same salt is obtained as a curdy dirty yellow hydrate, $AgBO^2 + \frac{1}{2}aq.$, on mixing concentrated solutions of nitrate of silver and monoborate of sodium, or boiling concentrated solutions of silver-salt and borax. It is decomposed by washing with water, especially if hot, which ultimately leaves nothing but oxide of silver.

Acid borates of silver have not yet been obtained pure. Rose states that cold concentrated solutions of nitrate of silver and borax yield a white precipitate containing $3Ag^2O$ to $4B^2O^3$, and after washing with a little cold water, which turns it brown, $4Ag^2O$ to $5B^2O^3$. According to Laurent, nitrate of silver yields with pentaborate of potassium, an acid borate of silver which decomposes partially in washing.

BORATES OF SODIUM.—Boric anhydride fused with excess of hydrate of sodium expels 3 at. water and forms *trisodic orthoborate*, Na^3BO^3.

$$B^2O^3 + 6NaHO = 3H^2O + 2Na^3BO^3$$

(Bloxam, Chem. Soc. Qu. J. xiv. 143). Fused with excess of carbonate of sodium at a bright red heat, it expels $1\frac{1}{2}$ at. carbonic anhydride and forms: $Na^6B^4O^9$ or $3Na^2O.2B^2O^3$.

$$2B^2O^3 + 3Na^2CO^3 = Na^6B^4O^9 + 3CO^2.$$

(Arfvedson, Gmelin's Handbook, iii. 87; compare Bloxam, Chem. Soc Qu. J. xii. 186). By fusing borax with excess of carbonate of sodium, Arfvedson found that 1 at. anhydrous borax expelled 3 at. carbonic anhydride producing a dibasic borate of sodium or tetrasodic borate: $Na^4B^2O^5$ or $2Na^2O.B^2O^3$:

$$Na^2O.2B^2O^3 + 3(Na^2O.CO^2) = 3CO^2 + 2(2Na^2O.B^2O^3),$$

1 at. carbonate of sodium fused with 1 at. boric anhydride yields *anhydrous monometaborate of sodium*, $NaBO^2$ or $Na^2O.B^2O^3$, and with 2 at. boric acid anhydride, it yields anhydrous acid borate of sodium, $Na^2B^4O^7 = Na^2O.2B^2O^3 = 2NaBO^2.B^2O^3$. The aqueous solutions of both these salts yield crystalline hydrates which might be regarded either as orthoborates or metaborates, but are most probably the latter. Respecting the behaviour of the tri- and tetrasodic borates in the hydrated state, nothing appears to be known.

Monometaborate or *Neutral Borate of Sodium*, $NaBO^2$, is produced by heating 62 pts. of crystallised boric acid, or 191 pts. crystallised borax, with 53 pts. of anhydrous carbonate of sodium at a heat near the melting point of silver. The unfused mass thus obtained dissolves in water, with rise of temperature; and by cooling the hot but not saturated solution, the hydrated salt $NaBO^2 + 4aq.$ (or possibly $Na^3BO^3 + 3aq.$) crystallises in large oblique rhombic prisms with lateral angles of 130° and 70°. It has a caustic alkaline taste, and quickly absorbs carbonic acid from the air, both in the solid state and in solution; but on boiling the solutions, the carbonic acid escapes. At 57° C. it melts in its water of crystallisation, and after the liquid has cooled for some time, the hydrate $NaBO^2 + 3aq.$ separate in indistinct crystals. At a stronger heat, it gives off all its water, and forms a friable tumefied mass, which absorbs carbonic acid from the air.

Dimetaborate or *Acid Metaborate of Sodium.* $Na^2B^4O^7 = 2NaBO^2.B^2O^3$, or *$NaO.2BO^3$*. *Biborate of Soda. Borax.*—This salt is obtained in the anhydrous state by fusing 124 pts. crystallised boric acid with 53 pts. anhydrous carbonate of sodium, or by heating crystallised borax. (A process for obtaining borax on the large scale by heating boric anhydride with carbonate of sodium has been patented by Sautter Nov. 20th, 1843). In contact with water, it passes into the hydrated state, and crystallises from its aqueous solution, either with 5 or with 10 at. water, according to the temperature. The former hydrate is octahedral borax; the latter, prismatic or ordinary borax.

Borax is found native in several localities, viz. at Halberstadt in Transylvania, at Viquintizoa and Escapa in Peru, in the mineral springs of Chambly, St. Ours, &c. Canada West, but more particularly in certain salt lakes of India, Thibet, and other parts of Asia, whence the greater part of the borax of commerce was formerly obtained. The salt separated from these waters by evaporation, either natural or assisted by artificial contrivances, is sent to Europe as crude borax or tincal, sometimes in large regular crystals, but more frequently as a white or yellowish-white mass, which is very impure, containing lime, magnesia, and alumina, and likewise covered over with a greasy substance (said to be added to diminish the risk of breakage during transport). According to analyses by Richardson and Browell, crude Indian borax contains:

Boric acid (anhydrous)	22·88	40·24	24·41
Soda ,,	12·59	11·11	11·71
Chloride of sodium	0·92	0·11	0·21
Sulphate of sodium	0·13	0·49	2·84
Sulphate of calcium	1·36	0·68	1·36
Insoluble matter	17·62	1·37	20·02
Water	44·50	46·00	39·45
	100·00	100·00	100·00

The purification or refining of this crude Asiatic borax has been carried on from very early times in various seaport towns of Europe, especially at Venice, and more lately at Amsterdam. Great pains have always been taken to keep the process secret, but two methods, one with *lime* and the other with *soda*, have become known:—1. The tincal is macerated in a small quantity of cold water, and stirred about, with gradual addition of 1 per cent. of slaked lime, the turbid lime-water being poured off from time to time, and when it has clarified, again poured upon the crystals. This treatment removes the greater part of the soapy compound, and the rest is decomposed by adding 2 per cent. of chloride of calcium to the solution of the crystals in hot water. The insoluble lime-soap thus formed, is removed by straining, and the clear liquid is evaporated to the density of 21° Beaumé.—2. The powdered tincal is placed in a tub with holes in the bottom, and washed with a solution of caustic soda of specific gravity 1·034, then drained and dissolved in water, and 12 per cent. of soda added to precipitate the earths, after which the solution is strained and evaporated. The crystallisation is effected in wooden vessels lined with lead, having the form of short inverted cones.

The greater part of the borax used in the arts, is now prepared in France by treating the native boric acid of Tuscany with carbonate of sodium, according to a method first practised by Payen and Cartier. 1300 kilogrammes of crystallised carbonate of sodium are dissolved in 1500 litres of water in a wooden vessel lined with lead; the liquid is heated to the boiling point by a jet of steam, and 1200 kilogrammes of crystallised boric acid are added. The density of the solution varies according to the degree of purity and dryness of the boric acid used; it is brought to a certain strength by adding borax or water as required, then left at rest till the insoluble matters have settled down, and finally transferred to the crystallising vessels, which are rectangular wooden boxes lined with lead, 6 metres long, 1·7 met. wide, and 0·5 met. deep. The formation of prismatic or of octahedral borax, depends upon the density of the solution, and the temperature at which the crystallisation takes place.

a. Prismatic or *Ordinary Borax*, $NaHB^2O^4 + \frac{9}{2}aq.$ or $2NaHB^2O^4 + 9aq.$ or $NaO.2BO^3 + 10aq.$—To obtain this hydrate, the solution, after all the carbonic acid has escaped, should have a density of 21° or 22° B. (specific gravity 1·14 to 1·15), and should boil at 104° C. (220° F.) It is left to crystallise for two or three days, the crystallisation being finished when the thermometer in the interior of the vessels stands at 25° to 30° C. (77° to 86° F.) The crystals thus obtained, are freed from mother-liquor, then dissolved in boiling water together with $\frac{1}{20}$ of their weight of crystallised carbonate of sodium, to separate any remaining earths, and the strained liquid is concentrated to 21° or 22° B. and left to crystallise as before. The mother-liquor is then drawn off as rapidly as possible with wide syphons, and that which remains amongst the angles of the crystals is soaked up with sponges, so that no small crystals may deposit upon the larger ones. The whole is then covered and left at rest for several hours, to avoid the formation of cracks in the crystals, which would be occasioned by the access of cold air.

The mother-liquor is diluted with water and used in a subsequent operation for dissolving the boric acid and carbonate of sodium. After three or four operations, it contains a considerable quantity of sulphate of sodium; but on cooling it to 30° C. (86° F.), borax crystallises out alone, the sulphate remaining in solution. The last mother-liquors yield by evaporation an impure borax, which is used in glass-making.

Considerable quantities of borax are also prepared from the native borate of calcium and sodium (*Boronatro-calcite*), from South America, by decomposing it with carbonate of sodium, either in the wet or in the dry way.

Artificial borax is for the most part purer than that obtained from native tincal by the refining process, but the crystals often contain cracks, and split when heated, in the direction of their natural cleavage, which is a great inconvenience when the borax is used for soldering, as it causes the crystals to fly off from the surface of the metal. This fault is partially corrected by slow recrystallisation from a rather concentrated solution; but it is more effectually remedied by the addition of a small quantity of tincal before recrystallisation. (For further details of the manufacture of borax, see *Ure's Dictionary of Arts, Manufactures, and Mines*, i. 379; *Handwörterbuch der Chemie*, 2^{te} Aufl. ii. [2] 320; *Précis de Chimie industrielle par A. Payen*, 4^{me} ed. i. 436.)

The impurities generally found in artificial borax, are carbonate of sodium, small quantities of sulphates, chlorides, and salts of calcium and magnesium. It is sometimes purposely adulterated with alum and common salt. It should dissolve in about 2 pts. of hot water, and exhibit no effervescence when treated with acids. The aqueous solution should remain perfectly clear on addition of alkali, and when acidulated with nitric acid, should not be clouded either by chloride of barium or nitrate of silver.

The proportion of soda in borax may be estimated by colouring the solution with litmus, and adding a standard solution of sulphuric acid, till a bright red colour is produced (p. 631), and from the amount of alkali thus determined, the quantity of boric acid may be calculated.

Prismatic borax forms large transparent prisms, of the monoclinic system, generally combinations of a nearly rectangular prism, having the acute and obtuse lateral edges truncated. The crystals effloresce in the air (according to Sims, only when they contain carbonate of sodium). When heated, they melt in their water of crystallisation, swelling up considerably, and solidifying to a loose spongy mass called burnt or calcined borax (*Borax usta*); at a red heat, the salt fuses to a colourless anhydrous glass of specfiic gravity 2·36, called vitrified borax. This, if pulverised and exposed to the air, gradually absorbs 10 at. water, reproducing ordinary prismatic borax.

β. *Borax with 6 at. water*, $Na^2O.2B^2O^3 + 6aq.$ or $NaHB^2O^4 + \frac{5}{2}aq.$ — Found by Bechi in an old lagoon crater; not yet obtained artificially.

γ. *Borax with 5 at. water. Octahedral Borax*, $Na^2O.B^2O^3 + 5aq.$ or $NaHB^2O^4 + 2aq.$ (or possibly $NaH^5B^2O^6$). — To obtain this salt, the solution (p. 646), is concentrated to a strength of 30° B (specific gravity 1·246), and left to cool very slowly in a warm place. The crystallisation begins at 79° C. (174° F.), and as soon as the temperature of the liquid has fallen to 56° C. the mother-liquor must be quickly withdrawn, because at that temperature prismatic borax begins to crystallise out. After a few hours, the crusts of the octahedral salt are removed and dried in the air. The crystals are regular, transparent octahedrons, harder and less fragile than ordinary borax; they have a conchoïdal fracture, and specific gravity = 1·8. They are unalterable in dry air, but in a moist atmosphere, they absorb water, and are converted into prismatic borax. When heated, they fuse to an anhydrous glass with less intumescence than common borax, and without splitting. On this account, octahedral borax is better adapted than common borax for many purposes, as for soldering and as a flux; its smaller proportion of water (30 per cent., that of common borax being 47 per cent.) also diminishes the cost of transport. Nevertheless, prismatic borax is generally preferred by consumers, probably because they are used to it, and it is sold at a lower price, weight for weight.

δ. *Amorphous Borax*, $NaHB^2O^4 + aq.$—Obtained by evaporating a solution of borax at 100° C.

Borax is easily soluble in water, but insoluble in alcohol. Poggiale found that 100 parts of water at various temperatures, dissolve the following quantities of prismatic borax:

at 0° C.	2·8 pts.	at 50° C.	27·4 pts.
10	4·6	60	40·4
20	7·9	70	57·8
30	11·9	80	76·2
40	17·9	90	119·7

and at the boiling heat, 201·4 parts.

The aqueous solution has a slight alkaline reaction, and changes the light yellow colour of an alcoholic solution of turmeric to brown: on adding a small quantity of sulphuric acid, the yellow colour is restored; but a larger addition of sulphuric acid sets the boric acid free, which then produces the peculiar red-brown colouring already mentioned (p. 639).

Borax is easily decomposed by acids. Even water, when present in considerable quantity, abstracts part of the base, so that a dilute solution of acid borate of sodium reacts like a mixture of boric and the neutral borate, or even free soda, giving, for example, a brown precipitate with silver-salts (p. 641). A solution of borax evaporated with excess of hydrochloric acid leaves a mixture of chloride of sodium and free boric acid. It also absorbs carbonic acid when exposed to the air, or when the gas is passed into it, and on adding alcohol to the liquid, when saturated with carbonic acid, no borax separates from it. A solution of borax saturated with sulphuretted hydrogen, and mixed with alcohol, separates, on addition of ether, into two layers, the lower containing sulphide of sodium, the upper free boric acid.

Borax forms with many of the weaker acids, double salts in which the boric acid appears to act as a base to the other acid. Thus, with *arsenious acid* it forms a compound whose empirical formula is $3Na^2O.6B^2O^3.5As^2O^3 + 10aq$. It unites also with fluoride of sodium (see p. 633). When 1 at. *tartaric acid* is mixed in solution with 2 at. borax, boric acid separates out on cooling; if the quantity of tartaric acid be gradually increased, the quantity of boric acid separated likewise increases up to a certain point; but beyond that it diminishes, and at last no further separation of boric acid takes place. Here also the boric acid seems to play the part of base towards the tartaric acid (see TARTRATES). *Acid tartrate of potassium* also forms a double salt with borax. Of silicic acid, a solution of borax dissolves but a mere trace.

Benzoic, *tannic*, and *gallic acids* dissolve in borax-solution more readily than in water. Many insoluble substances, *e.g. stearic* and other fatty acids, *colophony*, *shellac*, and other *resins*, dissolve in borax-solution as readily as in weak alkaline leys, the solution acting in fact just like a mixture of boric acid and free alkali.

At a red heat, on the other hand, the boric acid in borax readily unites with and dissolves metallic oxides, forming fusible double salts: hence the great use of borax in metallurgic and assaying operations, and for soldering. The compounds thus formed often take the form of transparent glasses of various colours, affording very characteristic and delicate tests for the several metals: hence the use of borax in blowpipe analysis. It is also used in the formation of easily fusible glass fluxes for enamels and glazes. An enamelled coating for cast-iron vessels is made by first fusing on the surface of the metal, a mixture of quartz, felspar, clay, and borax, and then covering it with a glaze containing borax. A glazing of 1 pt. clay, 1 pt. felspar, and 2 pts. borax is also used instead of lead-glazing for stone-ware.

Borax is likewise used, though not to any great extent, in medicine, either directly as a remedy, external or internal, or for the formation of pharmaceutical preparations, such as tartarised borax.

c. Tetrametaborate of Sodium. $NaH^3B^4O^8 + \frac{7}{2}aq.$—Produced by boiling 2 at. borax with 1 at. chloride of ammonium, as long as ammonia continues to escape:

$$2NaHB^2O^4 + NH^4Cl = NaH^3B^4O^8 + NaCl + NH^3.$$

It separates from the filtrate by slow evaporation in milk-white, transparent, shining, hard crystalline crusts; dissolves in 5 to 6 pts. water of mean temperature, forming an alkaline solution; yields a precipitate of boric acid on addition of a *dilute* acid, whereby it is distinguished from borax; melts when heated, with less tumefaction than ordinary borax. (Bolley, Ann. Ch. Pharm. lxviii, 122.)

d. Pentametaborate. $NaH^4B^5O^{10} + \frac{7}{2}aq.$—Prepared by dissolving 1 at. borax and 3 at. boric acid in hot water, and separates from the solution in small crystals aggregated in roundish masses; they do not suffer any loss of weight at 100° C., and give off their water of crystallisation but slowly at higher temperatures. The salt to which Laurent assigned the empirical formula $Na^{10}B^{48}O^{77} + 55aq.$ is perhaps this pentaborate.

e. Hexmetaborate. $NaH^5B^6O^{12}$.—Not yet obtained in the solid form, but perhaps contained in the solution produced by mixing 3 at. borax dissolved in water with 1 at. sulphuric acid:

$$3NaHB^2O^4 + H^2SO^4 = Na^2SO^4 + NaH^5B^6O^{12}.$$

This liquid thus formed does not redden litmus; but if 1 at. more of sulphuric acid be added, all the boric acid is set free, and the mixture exhibits the wine-red colour thereby produced, which, however, another drop of sulphuric acid immediately changes to bright-red (Laurent, Ann. Ch. Phys. [2] lxvii. 218). The hexborate is perhaps also formed when aqueous borax is mixed with boric acid till the liquid no longer exhibits a basic reaction. This solution is said to yield by evaporation tabular crystals, having a cooling taste like nitre, a neutral reaction, and giving off 30 per cent. water when melted. (Tünnermann.)

Borate of Sodium and Calcium. $NaCaH^2B^4O^8$ + 9 aq.—Such, with addition of 1·9 per cent. chloride of calcium, is, according to Helbig (Chem. Centr. 1858, p. 494), the composition of a mineral from South America, known in commerce as "borate of lime," and forming irregular nodules, mainly composed of a net-work of translucent crystals. Stein regards it as identical with the hydroborocalcite of Hayes and the boronatrocalcite (*q.v.*) of Ulex.

Borate of Sodium and Magnesium. $NaMg^2H^2B^6O^{10}$ + 14 aq. (Rammelsberg).—Separates by spontaneous evaporation, from a mixture of the cold aqueous solutions of borax and sulphate of magnesium, in large, shining, efflorescent, monoclinic crystals. It dissolves in cold water, forming an alkaline solution which is not precipitated by ammonia, but becomes turbid when boiled, clear again on cooling. If the liquid, after boiling for some time, be quickly filtered, the residue consists of basic borate of magnesium.

BORATES OF STRONTIUM. 1. *Orthoborate,* Sr^3BO^3.—Obtained by heating boric anhydride to redness with excess of hydrate or carbonate of strontium. (Bloxam, Chem. Soc. Qu. J. xii. xiv. 142.)

2. *Metaborates.*—The monoborate has not been obtained. Strontium-salts, precipitated by borax in the cold, yield a precipitate, which when pressed between paper and dried at 100° C., has the composition $Sr^3H^2B^5O^{10} + \frac{5}{2}$aq, gives off 2 at. water at 200°, and the rest at 300°, and is partially decomposed by hot water, the residue probably consisting of the sesquiborate, $Sr^2HB^3O^6$.

The *dimetaborate,* $SrHB^2O^4 + \frac{3}{2}$aq. (at 100° C.), is said to be precipitated from boiling solutions of borax and chloride of strontium. It has an alkaline reaction; dissolves in 130 pts. of pure water, more easily in presence of ammoniacal salts; gives off 3 at. H as water at 280°, the remaining atom at a red heat, leaving the anhydrous salt $Sr^2Br^4O^7 = Sr^2O.2B^2O^3$ ($= 2SrHB^2O^4 - H^2O$).

The *tetrametaborate,* $SrH^3B^4O^8 + \frac{3}{2}$ aq. is obtained, according to Laurent, by boiling the preceding with excess of boric acid, and evaporating the filtrate. Pentaborate of potassium also precipitates strontium-salts, but the precipitate has not been examined.

BORATE OF ZINC.—Sulphate of zinc, precipitated by borax in the cold, yields a precipitate consisting chiefly of *monoborate* of zinc, $ZnBO^2$, which, however, is decomposed by washing with cold water, leaving a basic salt $= 4ZnBO^2.5ZnHO + 2$ aq. (at 100° C.) A solution of a zinc-salt, mixed at the boiling heat with borax and boiled for some time, yields a precipitate consisting of a similar basic borate, mixed with basic sulphate of zinc.

Boric Ethers.

BORATES OF AMYL. a. *Orthoborate.* $(C^5H^{11})^3BO^3$ (Ebelmen and Bouquet, Ann. Ch. Phys. [3] xvii. 61).—Produced by the action of chloride of boron on amylic alcohol:

$$3(C^5H^{11}.H.O) + BCl^3 = 3HCl + (C^5H^{11})^3BO^3.$$

When vapour of chloride of boron is passed into amylic alcohol, hydrochloric acid is evolved, and the liquid quickly separates into two layers, the upper of which, when decanted and distilled, passes over almost wholly between 260° and 280° C., and when again rectified, yields pure tri-amylic borate. It is a colourless, oily liquid, having a specific gravity of 0·87 at 0° C., and a faint odour like that of amylic alcohol; it burns with a green-edged flame, and boils between 270° and 275° C. Vapour-density, by experiment, = 10·55; by calculation (2 vol.) = 9·45. Water decomposes it, yielding boric acid and amylic alcohol.

b. The *metaborate of amyl,* $C^5H^{11}BO^2$, has not yet been obtained.

c. *Acid borate,* $2C^5H^{11}BO^2.B^2O^3$ or $(C^5H^{11})^2O.2B^2O^3$ (Ebelmen, Ann. Ch. Phys. [3] xvi. 139), is obtained by pouring 2 pts. of amylic alcohol on 1 pt. of boric anhydride, heating the mixture to about 180° C., exhausting it with anhydrous ether, distilling off the ether from the decanted ethereal solution, and heating the residual liquid to 250—270° C., to free it from fusel-oil. The acid amylic borate thus obtained, is a clear, slightly yellowish liquid, having an odour like that of fusel-oil. It may be heated to 300° C. without alteration, but is decomposed at higher temperatures. It burns with a green flame.

When fusel-oil is heated to 300° C. with excess of boric anhydride, a colourless liquid passes over, which smells like amylic alcohol, and begins to boil below 100°; but the boiling point rises quickly, and there remains a vitreous mass, resembling the acid ether. As acid borate of methyl gives off oxide of methyl by dry distillation, it is probable that the lighter products of the distillation just mentioned contain oxide of amyl.

BORATES OF ETHYL. *a. Orthoborate.* $(C^2H^5)^3BO^3$. (Ebelmen and Bouquet, Ann. Ch. Phys. xvii. 55; Bowman, Phil. Mag. [3] xxix. 546.)—Prepared like the corresponding amyl-compound. Vapour of chloride of boron is rapidly absorbed by absolute alcohol, the liquid becoming hot and separating after a while into two layers, the lower of which is merely alcohol containing hydrochloric acid, while the upper contains the tri-ethylic borate, which may be separated by distilling the decanted liquid, with addition of a little alcohol, collecting that which passes over between 115° and 125° C., and rectifying. It is likewise produced by distilling a mixture of dry ethylsulphate of potassium and anhydrous borax. (H. Rose, Pogg. Ann. xcviii. 245.) See also vol. ii. p. 628.

It is a colourless, mobile liquid, having a peculiar, agreeable odour, and burning bitter taste. Specific gravity 0·885. It dissolves in all proportions in alcohol and ether, mixes with water, but is decomposed thereby in a few minutes, with separation of boric acid. Boiling point 119° C. Vapour-density (by experiment) = 5·14; by calculation (2 vol.) = 5·07. Burns with green flame, giving off white fumes of boric acid, and leaving no residue.

Metaborate, or *Neutral Borate*, $C^2H^5BO^2$.—Produced, with separation of boric acid, by the action of alcohol on the acid borate:

$$\underset{\text{Acid borate of ethyl.}}{2C^2H^5BO^2.B^2O^3} + \underset{\text{Alcohol.}}{C^2H^5.H.O} = \underset{\text{Metaborate of ethyl.}}{3C^2H^5.BO^2} + \underset{\text{Boric acid.}}{HBO^2}.$$

When the syrupy acid ether is mixed with absolute alcohol, boric acid separates, with considerable evolution of heat, and on separating the liquid therefrom by decantation and pressure, and heating it for a while to 100° C., boric acid is again deposited, and there remains a colourless mobile liquid, which resembles the orthoborate, and yields by analysis 32·93 per cent. carbon and 6·97 hydrogen, the formula requiring 33·38 C, and 6·96 H. (Handw. ii. [2] 309.)

Acid Borate. $2C^2H^5BO^2.B^2O^3 = (C^2H^5)^2O.2B^2O^3$. *Biborate of Ethyl* (Ebelmen, Ann. Ch. Phys. [3] xvi. 129.)—Produced by the action of boric anhydride on alcohol. When finely pulverised boric anhydride is mixed with an equal quantity of absolute alcohol at 18° C. the mixture becomes hot, quickly attaining the temperature of 50°, and begins to boil when heated to 95°. If the distillation be interrupted as soon as the boiling-point rises to 110°, the distilled portion poured back, and the distillation repeated till the boiling-point again rises to 110°, acid borate of ethyl remains in the retort, mixed with boric acid, from which it may be separated by digesting the residue for twenty-four hours with anhydrous ether, decanting from the undissolved portion, and distilling till the heat in the retort rises to 200°. Acid borate of ethyl then remains in the form of a thick yellowish liquid, which gives off white fumes in the air at 200°, and solidifies on cooling to a transparent glass. This glass is rather soft, even at mean temperatures, and at 40° or 50° may be drawn out into long threads. It has a faint ethereal odour, a burning taste, and blisters the skin, being at the same time converted into a white powder of boric acid. It gave by analysis, 19·8 per cent. C, 4·4 H, and 66·7 B^2O^3, the formula requiring 22·5 C, 4·7 H, and 65·3 B^2O^3.

Acid borate of ethyl begins to decompose at 300° C. with fusion, intumescence, and thickening, the products being ethylene-gas, alcohol-vapour, vapour of the undecomposed ether, vapour of water, and fused boric anhydride free from charcoal. The ethylene-gas burns with a green flame, the colour arising from admixed boric ether, which, however, may be removed by washing the gas with water.

The acid ether becomes very hot by trituration with *water*, being resolved into alcohol, and boric acid. Exposed to moist air, it becomes white on the surface from slow decomposition. It dissolves in *alcohol* and in *ether*, but gives off these liquids completely at 200° C., a portion of the undecomposed boric ether then passing over with the alcohol so that the distillate burns with a green flame, and when mixed with water solidifies from separation of boric acid. The syrupy acid ether treated with absolute alcohol in the manner above described, yields the neutral borate of ethyl.

BORATES OF METHYL.—a. *Orthoborate.* $(CH^3)^3BO^3$ (Ebelmen and Bouquet, Ann. Ch. Phys. [3] xvii. 59.)—Produced by the action of chloride of boron on anhydrous methylic alcohol; purified by rectifying the upper of the two resulting layers of liquid. It is a colourless mobile liquid of specific gravity 0·955; has a pungent odour somewhat like that of wood-spirit; boils at 72° C. Vapour-density = 3·66. Dissolves in alcohol and ether, is quickly decomposed by water, and burns with a green flame.

b. *Acid Borate* $2CH^3BO^2.B^2O^3 = (CH^3)^2O.2B^2O^3$ (Ebelmen, Ann. Ch. Phys. [3] xvi. 137.)—Obtained, like the acid ethylic borate, by treating boric anhydride with anhydrous methylic alcohol. The mass is repeatedly heated to 110° C., the distillate being each time poured back, the residue is treated with ether, and the decanted solution heated to 200°. Acid borate of methyl is thus obtained as a vitreous mass, soft and tenacious at ordinary temperatures. It burns in the air with a beautiful green flame; is decomposed by distillation into boric anhydride and oxide of methyl; and by water, into boric acid and methylic alcohol.

BORON, SULPHIDE OF. B^2S^3.—This compound, which is the analogue of boric anhydride, is formed by igniting boron in vapour of sulphur (Berzelius, Pogg. Ann. ii. 145) or in sulphuretted hydrogen; also by heating boron with sulphide of lead (Wöhler and Deville, Ann. Ch. Pharm. cv. 72), or by heating a mixture of boric anhydride and charcoal in vapour of sulphide of carbon (Frémy, Ann. Ch. Phys. [3] xxxviii. 819), or by strongly heating a borate in vapour of sulphide of carbon (Skoblikoff and Rudloff, Petersb. Acad. Bull. xii. 319). To obtain a pure product, boron is heated in sulphur vapour as long as that vapour continues to be absorbed by it. The action is slow, because the sulphide forms a crust round the boron.

Pure sulphide of boron is a white solid body, sometimes amorphous, sometimes crystalline. It has a pungent sulphurous odour, like that of chloride of cyanogen, or chloride of sulphur. Its vapour attacks the eyes. By itself it does not appear to be volatile, but it volatalises in sulphuretted hydrogen, like boric acid in vapour of water. Heated in a stream of hydrogen, it melts, and gives off a little sulphur, perhaps however, only when not quite pure. It decomposes water with great energy, forming boric and sulphydric acids, a decomposition to which, as already observed, the formation of boric acid in the Tuscan lagoons has been ascribed.

There appears also to be a persulphide of boron, produced by heating boron in sulphur-vapour till it takes fire, and then leaving it to cool in the vapour. When the product thus obtained is thrown into water, boric and sulphydric acids are formed, and milk of sulphur is deposited. (Berzelius.)

BORONATROCALCITE. $NaCa^2H^3B^6O^{12} + \frac{15}{2}$ aq.—Native borate of calcium and sodium, called also *Hydroboracite*, *Hayesin*, and *Tiza*. (See BORATES OF SODIUM, p. 649.)

BOTRYOGEN. *Red vitriol.*—A native ferroso-ferric sulphate from Fahlun in Sweden, occurring rarely in small oblique rhombic prisms, having the lateral faces inclined to each other at an angle of 119° 56′, and to the terminal faces at 113° 37′; more frequently massive and as a deposit on gypsum, sulphate of magnesium, ferrous sulphate, and iron pyrites. Translucent, with vitreous lustre. Dark hyacinth-red to ochre-yellow, Harder than gypsum. Specific gravity 2·039. Swells up before the blowpipe, giving off water and leaving ferric oxide. According to Berzelius, its formula is $3Fe^2O.2SO^3 + 3(Fe^4O^3.2SO^3) + 36H^2O$.

BOTRYOLITE. *Chaux boratée silicieuse concrétionée.* $2CaBO^2.Ca^2Si^2O^5 + 2$ aq. —A kidney-shaped mineral of delicate fibrous texture, found in the veins of magnetic iron ore at Arendal in Norway; generally as a deposit on crystals of calcspar. Its formula is the same as that of datolite, but with twice the amount of water.

BOULANGERITE. A tribasic sulphantimonite of lead, $3Pb^2S.Sb^2S^3$ or $\overset{\prime\prime\prime}{Sb}Pb^3S^3$, found at Molières in France, in Lapland, and other localities. Crystallo-laminar or fine-grained. Dark lead-grey. Specific gravity 5·59 to 5·97.

BOURNONITE. *Schwarzspiessglanzerz. Antimoine plombo-cuprifère:* $2Pb^2S.Cu^2S.Sb^2S^3 = \overset{\prime\prime\prime}{Sb}Pb^2CuS^3$.—Crystallises in right rectangular prisms of dark steel-grey colour, with metallic lustre, and yielding a black powder. Hardness equal to that of calcspar. Specific gravity 5·7 to 5·8. Melts before the blowpipe, giving off white fumes, covering the charcoal with oxide of lead, and changing to a slag containing a large quantity of copper. It is found in the copper mines of Cornwall, at Neudorf and Andreasberg in the Harz, at Kapnik and Offenbanya in Transylvania, &c., but is not very abundant. Some varieties found near Freiberg contain silver to the amount of about 0·12 per cent. (Gm. v. 486.)

BOVEY COAL. A kind of coal of a brown or brownish-black colour and lamellar texture, the laminæ being often flexible when first dug out, but generally hardening by exposure to the air. It consists of wood penetrated with petroleum or bitumen, and frequently contains pyrites, alum, and protosulphate of iron. By distillation, it yields a fetid liquor mixed with ammonia and an oil partly soluble in alcohol. It is found in England, France, Italy, Switzerland, Germany, Iceland, &c.

BOWENITE. See SERPENTINE.

BOYLE'S FUMING LIQUOR. *Monosulphide of Ammonium* (p. 193.)

BRAGITE. A mineral found at Arendal in Norway, but not yet sufficiently examined to establish its separate identity. (Forbes and Dahll, J. pr. Chem. lxvi. 446.)

BRAIN. See Nervous Tissue.

BRAN. *Son. Kleie.* (Millon, Ann. Ch. Phys. [3] xxvi. 5. Péligot, *ibid.* xxix. 5. Kékulé, Liebig's chem. Briefe, 3 Aufl. i. 595. Wetzel and Van Hees, Arch. Pharm. [2] lxvii. 284. Poggiale, Compt. rend. xxxvii. 171; xlix. 128. Sigle, Dingl. pol. J. cxxxi. 298. Mouriès, Compt. rend. xxxvii. 351; xlvii. 505; xlviii. 431. Oudemans, Rep. chim. app. i. 585.)—The husky portion of ground corn, separated by the boulter from the flour. The analyses which have been made of it, even from the same kind of corn, differ widely in the proportion of some of the essential constituents, as the following table will show.

	Rye-bran.	*Wheat-bran.*					
	Oudemans.	Oudemans.			Poggiale.	Kékulé.	Millon.
Ash	3·35	6·52	6·26	4·99	5·5	5·6	5·7
Water	14·55	14·07	14·27	14·40	12·7	13·8	13·9
Fat	1·86	2·46	2·88	3·88	2·9	4·1	3·6
Nitrogenous matter (gluten, &c.) .	14·50	13·46	12·68	15·41	13·0	67·3	14·9
Dextrin	7·79	5·52	5·24	5·71	7·9	4·1	51·0
Starch	38·19	26·11	29·74	29·31	21·7		
Sugar					1·9		
Cellulose	21·35	30·80	27·11	25·98	34·6	9·2	9·7
Resinous and odoriferous matter .							1·2
	101·59	98·94	98·28	99·68	100·0	104·1	100·0
Nitrogen	2·23	2·07	1·95	2·37			

Kékulé's determination of the nitrogenous matter is probably too high. The 13·0 per cent. nitrogenous matter found by Poggiale was made up of 5·6 soluble matter (albumin), 3·9 insoluble, but capable of assimilation, and 3·5 insoluble and incapable of assimilation. Poggiale isolated the cellulose by rendering the starch soluble with diastase; he finds that the usual process of determination by the successive use of acids and alkalis, always gives the amount of cellulose too low, part of it being converted by those reagents into sugar and dextrin.

Bran, though rich in nitrogen, appears to possess but little nutritive power. Animals fed upon it quickly lose flesh (Poggiale). It contains a nitrogenous principle called cerealin, analogous to diastase, and perhaps identical therewith, which possesses the power of quickly converting starch into dextrin and sugar. Mouriès found that 130 pts. of wheaten bread containing bran easily diffused through 520 parts of water when triturated therewith, and yielded 59·35 pts. of soluble and 69·75 pts. of insoluble matter, whereas the same quantity of bread not containing bran, was converted by trituration with water into a semisolid mass, and yielded only 9·03 per cent. soluble matter to 120·25 insoluble. This action of the bran on the flour commences in the kneading and baking, but is completed only in the stomach. (See Bread.)

Bran is used by calico-printers in the clearing process, for removing the colouring matters adhering to the non-mordanted parts of the maddered goods, as well as the dun matters which cloud the mordanted portions. (See *Ure's Dictionary of Arts, Manufactures, and Mines*, i. 383.)

BRANCHITE. C^9H^{16}.—A fossil hydrocarbon from the lignite of Mount Vaso in Tuscany. It is colourless and translucent, like Scheererite; melts at 75° C. but does not crystallise on cooling. It dissolves in alcohol. Specific gravity = 1·00. (Savi, Leonhard and Bronn's Jahrbuch, 1842, p. 459.)

BRANDISITE. See Clintonite.

BRANDY. This well known liquor is the spirit distilled from wine, and forms an extensive article of trade in the south of Europe. It is generally manufactured from white or pale-red wines, but often from inferior articles, such as the refuse wine and the marcs of the wine-press. Distillation of the wines is the only process necessary for procuring brandy: hence the richer the wine in alcohol, the greater will be the yield of brandy. Many circumstances, however, independent of the manufacture, influence the quality of the product. Thus, white wines do not always afford more alcohol than the red, but they yield a spirit of finer quality, because they contain more of the essential oil of grapes. Wines which have a certain taste of the soil, communicate it to the brandy derived from them by distillation; thus, the wines of Selleul in Dauphiné give a brandy which has the odour and taste of the Florentine iris; those of St. Pierre in Vivarais, give a spirit which smells of the violet, and so of many other varieties.

Real Cognac is obtained from the distillation of choice wines, every attention being paid to the proper degree of cleanliness in the various utensils employed. In the improved form of still, a very superior article is obtained from inferior wines, but the small proportion of essential oils in such wines divests the brandy of that aromatic flavour which belongs to the better sorts of wine, and is communicated to the brandies procured from them. An inferior brandy called *eau-de-vie de marcs* is obtained by distilling the dark red wines of Portugal, Spain, and other wine-growing countries, also the lees deposited by wine in keeping, the marc or refuse of the grapes from the wine-press, the scrapings of wine-casks, &c.

Brandy, as sold in France, is generally of two strengths, designated as *à preuve de Hollande*, and *à preuve d'huile*, the former varying from 18° to 20° Beaumé. The stronger liquors are valued according to the quantity of *eau de vie à preuve de Hollande* that a given quantity will furnish on the addition of the proper quantity of water. These strengths are usually twelve, viz. of *five-six*, *four-five*, *three-four*, *two-three*, *three-five*, *four-seven*, *five-nine*, *six-eleven*, *three-six*, *three-seven*, *three-eight*, and *three-nine*, but the last is rarely made. The meaning of these strengths is as follows: — If a spirit be *five-six*, 5 pts. of the spirit will give a liquor *à preuve de Hollande*, when added to six measures of water. The spirit five-six has a specific gravity of 0·9237 or 22° Bm.; but all the other strengths are variable, on account of the uncertainty of the strength of the spirit *à preuve de Holland*.

The following is an average of the yield of brandy which some wines afford by distillation:

1000 litres of wine of St. Gilles, in the environs of Montpellier, afford

of three-six brandy	150 litres
„ of good wine of calcareous soils	140 „
„ of wines of fertile soils near Montpellier	100 „
„ of wines of soils producing much grapes	100 „

Wines of the countries nearest the Mediterranean furnish the largest proportion of brandy, which diminishes as the grapes grow in more northern countries.

British brandy is an artificial product fabricated by the rectifying distiller. The following receipt is given by Ure: — "Dilute the pure alcohol to the proof pitch, and add to every hundred pounds weight of it from half a pound to a pound of argol—crude tartar—dissolved in water, some bruised French plums, and a quart of good cognac. Distil this mixture over a gentle fire in an alembic provided with an agitator. The addition of brandy and argol introduces œnanthic ether, and if a little acetic ether be added to the distillate, the whole imparts the peculiar taste of genuine Cognac brandy. Colour with burnt sugar if necessary, and add a little tannic acid to impart astringency." (See *Ure's Dictionary of Arts, Manufactures, and Mines*, i. 389; also *Muspratt's Chemistry*, i. 103.)

BRASS. An alloy of copper and zinc. (See COPPER; also *Ure's Dictionary of Arts, Manufactures, and Mines*, i. 399.)

BRASSICA. A genus of cruciferous plants, including some of the most important fodder plants and culinary vegetables, viz. the cabbage, rape, and turnip.

1. *Brassica oleracea.* Cabbage.—Of this species, many varieties are cultivated for their leaves, *e.g.* the common red or white cabbage (*Br. ol. capitata*), the Savoy cabbage (*Br. ol. bullata*), curled kale (*Br. ol. acephala*), &c. The turnip-stemmed cabbage, or kohl-rabi (*Br. ol. caulorapa* or *napobrassica*), is much cultivated in France and Germany for its fleshy turnip-like stem or bulb, which makes an excellent vegetable dish. Cauliflower and broccoli are also varieties of *Brassica oleracea*.

Fresh white cabbage-leaves contain 0·2 per cent. nitrogen; the dried leaves 3·7 per cent. (Boussingault, Ann. Ch. Phys. [2] lxviii. 337). Table A exhibits the composition of cabbage leaves as determined by Anderson (Chem. Centr. 1856, p. 232).—*a.* Of the young plant before the heart-leaves are formed. *b.* The outer leaves of perfectly ripe cabbage. *c.* The heart-leaves of the same.

TABLE A.—*Composition of Cabbage-leaves.*

	a	*b*	*c*
Albuminous substances	2·1	1·6	0·9
Woody fibre, gum, and sugar	4·5	5·0	4·1
Ash	1·6	2·2	0·6
Water	91·8	91·1	94·4

According to Sprengel (J. techn. Chem. xiii. 485), white cabbage contains, in the air-dried state, 52·5 per cent. water, 19·3 per cent. matter soluble in potash-ley, 25·6 per cent. woody fibre, besides wax, chlorophyll, &c. The ash of cabbage has been analysed by Way and Ogston (Journ. Roy. Agr. Soc. vii. [2] 593; xi. [2] 512), by Sprengel and by Stammer (Ann. Ch. Pharm. lxx. 294).

The fleshy stem or bulb of the kohl-rabi contains, according to Sprengel (*loc. cit.*) 91 per cent. water, the leaves 86 per cent. water. 100 pts. of the dried substance contain 41·4 pts. soluble in water, 38·2 soluble in potash-ley, 18·5 woody fibre, besides wax, fat, &c. The ash of the corms and leaves has been analysed by **Sprengel**, and by **Way** and **Ogston** (*loc. cit.*)

The ashes of the heart of cauliflower (*Br. ol.* var. *botrytis cauliflora*), and of the root and leaves of broccoli (*Br. ol.* var. *botrytis asparagoïdes*) have been analysed by **Th. Richardson**, Ann. Ch. Pharm. lvii.; Anhang zum dritten Heft).

TABLE B.—*Ash of different Varieties of Brassica oleracea.*

	Way and Ogston.		Sprengel.	Stammer.	Way and Ogston.		Sprengel.		Richardson.		
	Cow Cabbage		*White Cabbage*		*Kohl rabi*				*Cauliflower*	*Broccoli*	
	Leaves.	Stalk.			Bulbs.	Leaves.	Bulbs.	Leaves.	Hearts.	Root.	Leaves.
Ash in 100 pts. of fresh plant	0·7	1·2	—	—	—	—	0·95	2·60	0·71	1·01	1·70
" " " air-dried plant	—	—					—	—			
" " " plants dried at 100° C.	10·0	—	7·55	11·62	7·05	12·90	8·09	18·54			
Composition of ash in 100 pts.:											
Potash (anhydrous)	40·9	40·9	31·3	48·3	37·6	17·8	36·3	9·3	47·16	34·39	22·10
Soda "	2·4	4·0	12·0	—	13·3	8·1	2·8	—	—	14·79	7·55
Lime	15·0	10·6	23·1	12·6	11·1	34·2	10·2	30·3	4·70	2·96	26·44
Magnesia	2·4	3·8	0·3	3·7	4·0	3·2	2·3	3·6	3·93	2·38	3·43
Alumina	—	—	0·2	—	0·5	0·2	—	—	—	—	—
Ferric oxide	9·8	0·4	0·1	1·8	0·5	0·9	0·4	5·5	—	—	—
Sulphuric anhydride	7·3	11·1	12·7	8·3	12·6	14·0	11·4	10·6	11·16	10·35	16·10
Silicic "	10·6	1·0	2·8	0·4	6·7	7·1	0·8	9·6	1·92	0·65	1·83
Carbonic "	16·7	6·3	—	—	—	—	10·2	9·0	—	—	—
Phosphoric "	12·5	19·6	10·4	16·9	5·8	5·4	13·5	9·4	25·84	24·83	16·62
Calcic, magnesic, and ferric phosphates	—	—	—	—	—	—	—	—	3·67	2·12	6·21
Chloride of potassium	—	—	—	9·3	—	—	—	6·0	—	6·22	—
" " sodium	trace	2·1	6·0	—	6·1	7·8	11·9	6·7	2·78	trace	—

2. *Brassica Napus.*—Winter rape, Coleseed, and *Br. campestris* var. *oleifera*, Summer rape, Colzat or Colza, are cultivated chiefly for their seeds, which yield a large quantity of oil, and for the succulent food which their thick fleshy stems and leaves supply to sheep when other fodder is scarce. The cake which remains after the oil has been pressed from the seed, is used on the continent as food for cows and pigs, and also as a manure, for which purpose large quantities of it are imported into England. Colza or summer rape yields the largest quantity of oil, but winter rape is said to be hardier, and is therefore more generally cultivated in this country. **Way** (Journ. Roy. Agr. Soc. x. part 2) found, in 100 pts. of the dry seed of dwarf rape, 4·2 per cent. nitrogen, 37·8 fat, 3·3 ash, and 6·5 water. Of the ash of the seed and straw of rape, numerous analyses are given in Liebig and Kopp's *Jahresbericht für Chemie* for 1849, tables D and E to page 656. From these we extract the following:

TABLE C.—*Ash of the Seed and Straw of Brassica Napus.*

	Liebig,	Erdmann,	Rammelsberg,	Weber,	
	Seed.	Seed.	Seed.	Seed.	Straw.
Ash in 100 pts. of air-dried plant	—	—	—	2·39	3·41
" " " plant dried at 100° C.	5·19	4·03	4·44		
Composition of ash in 100 pts.:					
Potash	22·5	22·7	25·7	22·9	24·9
Soda	0·2	—	—	—	6·5
Lime	11·8	14·6	13·2	17·3	32·8
Magnesia	11·1	12·0	11·6	15·5	5·4
Ferric oxide	1·7	0·6	0·6	0·7	1·7
Sulphuric anhydride	6·7	0·5	0·5	0·5	1·2
Silicic "	6·0	1·1	1·1	2·0	4·1
Carbonic "	—	—	—	—	14·7
Phosphoric "	39·1	47·0	47·0	41·6	4·5
Chloride of potassium	—	—	—	—	2·1
" sodium	0·8	—	—	—	—

3. *Brassica Rapa*, the common white turnip, and *Br. campestris* var. *rutabaga*, or *napobrassica*, the swede turnip.—The ashes of these plants have been examined by **T. J. Herapath** (Chem. Soc. Qu. J. ii. 14), **Eggers** (Jahresber. f. Chem. 1849, p. 656); **Baer** (*ibid.* 1851, p. 710); **Stammer** (Ann. Ch. Pharm. lxx. 295); and **Way** and **Ogston** (*loc. cit.*).

TABLE D. — *Composition of Turnip-ash.*

	Herapath.		Way and Ogston.							Baer.		Stammer.	Eggers.
	Swede	*White*	*Swede*		*Dale's Hybrid*		*Green-topped white*						
	Bulbs	Bulbs	Bulbs	Leaves.	Bulbs.	Leaves.	Bulbs.	Leaves.	Seed.	Seed.	Straw.	Bulbs.	Oil-cake.
Ash in 100 pts. of fresh plant	1·23	0·65	0 75	1 97	1·09	1·19	0 59	1·82	3·67			0·46	5·70
Ash in 100 pts. of air-dried plant	—	—	—	—	—	—	—	—	—	4·58	4 41		
Ash in 100 pts. of plant dried at 100° C.	—	—	6·00	16·40	8·41	10·80	7·40	15·20	3·98	—	—	7·00	6·13
Composition of the ash in 100 pts.:													
Potash	62·6	47·9	23·7	11·16	36·9	13·5	48·5	12·7	21·9	16·1	16·5	46·5	21·9
Soda	trace	—	14·7	12·4	8·0	4 6	—	—	1·2	1·1	1·3	—	—
Lime	6·9	14·7	11·8	28·5	6·5	35·1	6·7	28·7	17·4	11·3	25·4	13·1	8·6
Magnesia	2·5	2·4	3·3	2·6	2·5	1·7	2·3	2·8	8·7	10·4	11·0	1·6	14·7
Alumina	trace	—	—	—	—	—	—	—	—	0·5	0 2		
Ferric oxide	0·25	trace	0·5	3·0	0·1	0·6	0·6	0·8	1·9	1·0	1·2		4 5
Sulphuric anhydride	4 2	2·6	16·1	10·4	11·7	6·7	12·8	7·8	7·1	7·9	5·5	9·9	1·6
Silicic "	0·1	1 2	2·7	8·0	2·7	1·2	0·9	2·0	0·7	9·9	3·4	1 0	13·1‡
Carbonic "	—*	—	10·7	6 2	12·6	13·8	14·8	14·6	0·8	6·9	27·6		2·1
Phosphoric "	15·9	16·6	9·3	4·9	8·8	4·6	7·6	3·1	40·1	34·0	4·0	15·5†	32·7
Chloride of potassium	} 7·4	—	—	—	—	—	—	15·5	—	—	—	10·6	0 2
" sodium		14·6	7·1	12·4	10·0	18 0	5·4	10 7	—	0·8	3·2	—	0·5

BRASSIC ACID. Colza oil is, according to Websky (J. pr. Chem. lviii. 449), a mixture of two glycerides, which yield by saponification, brassic acid, which is solid at ordinary temperatures, melts between 32 and 33° C., and crystallises from alcohol in long needles; and another acid, which is liquid at ordinary temperatures and resembles oleic acid. The two acids are easily separable by means of their lead-salts, the salt of the oily acid being soluble in ether, while brassate of lead is insoluble. Websky assigns to brassic acid the formula $C^{46}H^{44}O^4$. Städeler (Ann. Ch. Pharm. lxxxvii. 133) proposes $C^{44}H^{42}O^4$, or $C^{22}H^{42}O^2$, which agrees quite as well with the analyses, and is the same as that of erucic acid, extracted by Darby from oil of mustard. Brassate of sodium gives by analysis 8·5 per cent. soda; the formula $C^{22}H^{41}NaO^2$ requires 8·6 per cent.

BRAUNITE. Native sesquioxide of manganese. See MANGANESE.

BRAUNSTEIN. The German name of peroxide of manganese.

BRAYERA ANTHELMINTICA (Kunth), or *Hagenia abyssinica* (Lamarck). —The flowers of this plant, called *Kusso* or *Kosso*, contain, according to Viale and Latini (Correspond. Scient. in Roma, Nov. 1852), a peculiar acid, *hagenic acid*, in combination with ammonia.

Harms (Arch. Pharm. [2] lxxxviii. 165) found in 100 pts. of the ash of kusso, after deducting sand and charcoal:

CO^2	SO^3	P^2O^5	SiO^2	$Fe^4O^3.P^2O^5$	NaCl
13·58	1·90	14 43	3·14	5·50	7·38
Al^4O^3	Mg^2O	Ca^2O	Na^2O	K^2O	Mn^3O^4
1·97	6·43	13·37	13·41	18·89	trace

BRAZIL WOOD. The tree which yields this wood, the *Cæsalpina crispa*, grows in Brazil, and also in the Isle of France, Japan, and elsewhere. There are several varieties, distinguished by the names of the localities from which they are obtained, as Pernambuco, Lima, Santa Martha, Sapan (from Japan), &c. Pernambuco wood and Lima wood contain the largest amount of colouring matter; viz. about 2·7 per cent.; Sapan wood, only about 1·5 per cent. Peach or Nicaragua wood, sometimes called Santa Martha wood, is still inferior in point of quantity, but is preferred for some purposes.

Brazil wood is heavier than water, very hard, and susceptible of a good polish. Its colour is pale when newly cut, but becomes deeper by exposure to the air. The heaviest specimens generally yield the best colour. It has a sweetish taste when chewed, and is distinguished from red sanders or sandal wood by giving out its colour to water, which sandal wood does not. The colouring matter may also be extracted by alcohol or ammonia, and with greater facility than by water. The spirituous tincture, according to Dufay, stains warm marble of a purplish red, which, on increasing the heat, becomes violet; and, if the stained marble be covered with wax and

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* In the calculation of Herapath's analysis, the carbonic acid is deducted.

† Mixed with sand.

‡ And 1·5 basic ferric phosphate.

considerably heated, it changes through all the shades of brown, and at last becomes fixed of a chocolate colour.

According to Chevreul (Ann. Chim. lxvi. 226), the red colouring matter of Brazil wood, to which he gives the name *Brazilin*, exists ready formed in the wood, and is simply dissolved out by water or other solvents. To prepare it, the wood is exhausted with warm water; the solution evaporated to expel free *acetic acid*; the dry residue is dissolved in water; the liquid shaken up with oxide of lead, to remove any remaining free acids; the filtrate again evaporated to dryness; the residue dissolved in alcohol, the alcoholic solution likewise evaporated; the residue dissolved in water, and the solution treated with gelatin to precipitate tannic acid: lastly the evaporation and solution in alcohol must be repeated to remove the excess of gelatin. (Chevreul.)

Brazilin crystallises by spontaneous evaporation in reddish yellow needles. It is soluble in water, alcohol, and ether. The solutions have a fine red colour, if they do not contain free acid; but the addition of sulphuric, nitric, or hydrochloric acid changes the colour to dirty yellow; hydrofluoric acid turns it first yellow then greenish grey; phosphoric and citric acids give it a fine and permanent yellow colour, whereas with acetic acid a yellowish-red solution is formed, which when evaporated in contact with the air, leaves a residue of a fine red colour. The yellow produced by citric acid is well adapted for dyeing wood or silk.

By sulphydric, sulphurous, hyposulphuric, and boric acids, the colouring matter is bleached and destroyed; a similar action is exerted upon brazilin by zinc and dilute acids.

Alkalis change the red colour of a solution of brazilin to violet or blue: hence infusion of Brazil wood may be used as a test for these bases; with hydrate of alumina it forms a crimson lake; with tin- and lead-salts, purple precipitates. (Chevreul.)

According to Bolley (Zeitschr. Ch. Pharm. viii. 192), brazilin is identical with sapan-red, the colouring matter of Sapan-wood (*Cæsalpinia echinata* or *C. Sapan*), and is obtained therefrom with much greater facility than from Brazil wood. (See SAPAN RED, vol. v. p. 191.)

The precipitates obtained with an aqueous decoction of Brazil wood, are extensively used for dyeing and for staining paper for walls. The solubility of the colouring matter of Brazil wood, and its strong affinity for mordants, give it a very extensive range of application both in dyeing and in calico-printing. (For details respecting the mode of dyeing with Brazil wood, see *Muspratt's Chemistry*, vol. i. p. 573, and *Ure's Dictionary of Arts, Manufactures, and Mines*, vol. i. p. 397.)

BREAD. Bread consists of the flour of wheat or other cereal grain, kneaded with water into a paste or dough, which is rendered porous by the interpenetration of carbonic acid gas, either generated within the mass of the dough by fermentation, or forced into it by mechanical means. The dough having thus acquired the proper degree of porosity, is exposed to the heat of an oven, whereby the enclosed gas is further expanded, its escape being prevented by the simultaneous formation of the crust. The crumb of the bread thus produced is a soft porous mass of swollen, but otherwise unaltered starch, mixed with vegetable fibrin; in the crust, the starch is mainly converted into dextrin and empyreumatic products.

It is the rising of the dough, produced by the carbonic acid, which gives to well made bread its peculiar lightness, and distinguishes it from the close, heavy cake, produced by merely mixing flour with water and baking it. The usual method of generating the carbonic acid is by fermentation, and the manner in which this process is conducted has great influence on the quality of the bread; as, if it be not carried far enough, the dough will not rise sufficiently, and if allowed to go too far, it gives rise to the formation of acid and other objectionable products. To facilitate the understanding of it, we must give some account of the composition of flour.

The flour of all cereal grains consists of an azotised portion, chiefly vegetable fibrin; a non-azotised portion, chiefly starch, with variable quantities of dextrin and sugar; and inorganic salts, chiefly phosphates.

If moistened wheat flour be kneaded into a stiff paste, and well washed with water, a milky liquid runs off, and a viscid elastic solid, called gluten, is left behind. The milky liquid, if left to stand, deposits a quantity of starch mixed with minute particles of gluten, and the clear liquid filtered from the deposit, leaves on evaporation, a quantity of extractive matter, consisting of vegetable albumin, dextrin, glucose, or grape-sugar, possibly also gum, and other similar proximate principles, besides soluble inorganic salts. The gluten, which is essentially the flesh-forming constituent of the flour, consists of vegetable fibrin, held together by a very tenacious nitrogenous substance, called *glutin* or *gliadin*, which may be extracted by alcohol; it also contains small quantities of fat, and fine particles of bran mechanically mixed. It is the gliadin which gives to the nitrogenous portion of wheat-flour its peculiar adhesiveness, and causes the dough prepared with it to rise into a spongy mass when penetrated by gases. Other cereal grains, oats and rye for example, though rich in vegetable fibrin, contain scarcely any gliadin, and consequently the dough prepared from them possesses but little tenacity. This is the chief cause of the great superiority of wheat over all other cereals, for the preparation of bread.

When flour in the moist state is exposed to the air, the nitrogenous matter quickly passes into a peculiar state of decomposition, in which it is capable of acting as a ferment, converting the starch into dextrin and glucose, and the glucose into alcohol and carbonic acid (see FERMENTATION). Hence a portion of dough which has been left till it undergoes partial decomposition, and in which state it is called leaven, is capable of inducing the so-called *panary*, but really *alcoholic* fermentation, in a much larger quantity of dough, when well kneaded with it. "A little leaven leaveneth the whole lump." This method of bread-making has been practised from the oldest times, and is still the only one in use for the coarser kinds of bread, such as the *Schwarzbrot*, or black bread of Germany; but for the finer sorts, beer-yeast is now used as a substitute, or rather as a partial substitute of leaven. The process generally adopted in this country is as follows: A certain quantity of flour is mixed with yeast, salt, and tepid water. This constitutes the "sponge," which is covered up and set aside in a warm place, to undergo fermentation. In the course of an hour or so, the mass swells up considerably from the generation of carbonic acid, large bubbles of which rise to the surface and burst. With each successive burst, a sudden falling of the sponge takes place, followed by a gradual rising, and these alternate actions would, if allowed, continue for many hours. Various other modes of making an active sponge are employed, particularly by the use of potatoes. When the sponge, no matter how formed, is in an efficient condition, the baker mixes up with it fresh portions of flour, salt, and water, the quantities so added forming the greater part of the dough. The whole is then subjected to a thorough kneading with the hands, or sometimes with the feet, so that the fermenting dough may permeate and affect the entire substance, and thus cause an equable liberation of carbonic acid in every particle. The dough is set aside for a few hours, during which the fermentation proceeds, then kneaded a second time, and weighed out into loaves, which are allowed to continue fermenting till they have doubled their original bulk. They are then baked in the oven, within which they undergo a further increase of size, due chiefly to the expansion by heat of the confined gases: for the heat of the oven quickly arrests the fermentation.

In Paris, where bread-making has been brought to a high degree of perfection, the fermentation is produced chiefly by the gluten of the dough, yeast being used merely to facilitate the action. A lump of dough remaining from the last batch of bread, and consisting of 8 lbs. flour and 4 lbs. water, is left to itself for ten hours: in this state it is called fresh leaven (*levain de chef*). By kneading this with another quantity of 8 lbs. flour and 4 lbs. water, the once-revived leaven (*levain de première*) is obtained. After another interval of eight hours, 16 lbs. of flour and 8 lbs. water are added, forming the twice-revived leaven (*levain de seconde*); and after three hours more, 100 lbs. flour and 52 lbs. water containing $\frac{1}{4}$ to $\frac{1}{3}$ lb. beer-yeast are added, forming the finished leaven (*levain de tout point*). The 200 lbs. leaven thus obtained are mixed, after two hours, with 132 lbs. flour and 68 lbs. water, containing $\frac{1}{2}$ lb. of yeast in suspension and 2 lbs. common salt dissolved. This quantity of dough serves for five or six bakings. For the first baking, half the dough (200 lbs.) is made into loaves of the required size and form, which are exposed for a while in shallow baskets, to a temperature of 25° C. (77° F.), and then transferred to the oven. The bread thus obtained has a sourish taste and dark colour. The remaining half of the dough is again mixed with 132 lbs. flour, 70 lbs. water, $\frac{1}{2}$ lb. yeast, and the requisite quantity of salt; the half of this quantity of dough is then formed into loaves, left to ferment, and baked. The same operations are repeated three times, one-half of the dough being each time mixed with 130 lbs. flour, $1\frac{1}{3}$ lb. yeast, and the proper quantity of water and salt. The last stage yields the finest and whitest bread.

In the normal process of bread-making, the carbonic acid, whose evolution gives lightness to the bread, is derived principally, if not wholly, from the fermentation of the sugar of the flour, induced by the action of metamorphic gluten. But flour, as already observed, contains other nitrogenised substances than gluten, and other non-nitrogenised substances than sugar. Now these nitrogenous substances, the albumin, for example, readily undergo transformation, and then act as ferments, not only upon sugar and dextrin, but also upon starch, transforming it into dextrin and sugar, and sometimes also into lactic acid. This is the process which takes place in the germination of grain, in malting for example (p. 328), by the action of the albumin in the peculiar state called *diastase*. Now when wheat has been too much exposed to damp during harvesting, or has sprouted from any subsequent cause, or when the flour even of well-harvested wheat is exposed to heat and moisture, the albumin passes into this peculiar state, and the flour becomes incapable of yielding good bread, because, during the process of bread-making, the conversion of starch into dextrin and sugar, which always occurs to a slight extent, then takes place in an exaggerated degree. Bread made from such flour, is sticky, saccharine, and soddened, never light and porous. The conversion of the starch into dextrin and sugar likewise renders the bread darker in colour. In fact, the brown colour of wheaten bread made from flour containing fine bran, is due, not to admixture of particles of bran, but in great part at least to a conversion of the starch into dextrin and sugar by the action of the altered albuminous matter in the bran. According to Mège-Mouriès, bran contains a peculiar nitrogenous body called *cerealin*, which is specially active in inducing this conversion: it appears, however, to be identical or nearly identical, with ordinary diastase. Be this as it may, it is certain that the finest wheat flour obtained from the central portion of the grain, which contains but little nitrogenous matter, has very little tendency to undergo the change under consideration; but coarse flour obtained from the exterior of the grain, is rich in azotised substances, and more ready to undergo the glucosic deterioration. In white bread of good quality, the starch has undergone very little alteration. A small portion of it is rendered soluble in water, but the greater number of the granules are simply swollen, not burst, and may be washed out of the bread, collected, and weighed. Vogel gives the following analysis of a wheat-bread loaf: sugar, 3·6 per cent.; altered starch, 18·0; unaltered starch, 53·5; gluten, with some starch, 20·7 = 95·8.

The injurious action of diastase, &c. on starch in the process of bread-making, may be prevented by the addition of certain mineral substances. Alum has long been employed for this purpose by bakers, and it certainly has the effect of rendering available for bread-making many qualities of flour, which must otherwise be wasted. Dr. Odling says (Journal of the Society of Arts, April 9, 1858): "If we mix a solution of starch with infusion of malt, in the course of a few minutes only, the starch can no longer be detected, being completely converted into dextrin and sugar, but the addition of a very small quantity of alum prevents altogether or greatly retards the transformation. The action of diastase on undissolved starch is very gradual, but here also the interference of the alum is easily recognisable. Bread made with infusion of bran or infusion of malt, is very sweet, sodden, brown-coloured, and so sticky as almost to bind the jaws together during mastication. But the addition of alum to the dough causes the loaves to be white, dry, elastic, crumbly, and unobjectionable, both as to taste and appearance. I have found that flour which is of itself so glucogenic as to yield bread undistinguishable from that made with infusion of malt, could, by the addition of alum, be made to furnish a white, dry, eatable loaf."

Alum is also said to prevent bread from turning sour and mouldy. The sourness often observed in bread of inferior quality, arises from the conversion of part of the starch into lactic acid. Now as alum prevents the transformation of starch, it may be expected also to interfere with the production of lactic acid.

Considerable discussion has taken place as to the probable effects of the habitual use of alumed bread on the digestive functions, some medical men asserting that alum, unless taken in much larger quantity than is likely to occur in bread, is quite harmless, while others attribute to it the most injurious effects. In this, as in many cases, the truth probably lies in the middle. Many of the statements which have been put forth on this, as on other questions relating to the adulteration of food, are doubtless grossly exaggerated; nevertheless, it would be unsafe to assert that the use of alum is quite free from objection. Dr. Dauglish, in a paper to which we shall have again to refer, says: "Its effect on the system is that of a topical astringent on the surface of the alimentary canal, producing constipation, and deranging the process of absorption. But its action in neutralising the efficacy of the digestive solvents, is by far the most important and unquestionable. The very purpose for which it is used by the baker, is the prevention of those early stages of solution which spoil the colour and lightness of the bread whilst it is being prepared, and which it does most effectually: but it does more than needed: for whilst it prevents solution at a time that is not desirable, it also continues its effects when taken into the stomach, and the consequence is, that a large portion of the gluten and other valuable constituents of the flour, are never properly dissolved, but pass through the alimentary canal without affording any nourishment whatever."

Another objection made against the use of alum, viz. that it has the power of causing bread to retain a larger proportion of water than it otherwise would, so that bakers who use alum defraud their customers by selling water instead of bread, does not appear to rest on satisfactory evidence. Odling (*loc. cit.*) examined the new crumb of eighteen alumed and seven non-alumed loaves, and found that the former contained on the average 43·68 per cent., and the latter, 42·78 per cent. water, the difference being quite insignificant as compared with the differences between the individual loaves, whether alumed or not. The detailed results, together with the proportions of nitrogen and ash in the loaves, are given in the following table, the samples marked with an asterisk being the *non*-alumed loaves. They are interesting in a general point of view, independently of the alum question. The loaves were new, that is, obtained during the day on which they were baked.

Percentage of WATER, NITROGEN *and* ASH, *in Bread Alumed and Non-alumed.*

	Price in Pence.	Percentage of Water.	Percentage of Organic Matter.	Percentage of Mineral Matter or Ash.	Percentage of Ash in dry Bread.	Percentage of Nitrogen in new Bread.	Percentage of Nitrogen in dry Bread.
1	4¾	43·03	55·48	1·49	2·61	1·83	3·21
2	3½	42·86	56·07	1·07	1·87	1·47	2·57
3	3½	44·81	53·74	1·45	2·62	1·89	3·42
4	3½	46·71	52·12	1·17	2·19	1·14	2·13
5	4	45·42	53·24	1·34	2·45	1·66	3·05
6	4	44·33	54·29	1·38	2·47	1·04	1·88
7*	4	44·41	54·38	1·21	2·17	1·06	1·90
8	3¾	38·62	59·79	1·59	2·58	1·15	1·47
9*	3¾	42·77	56·00	1·23	2·15	1·31	2·29
10	4	43·67	55·09	1·24	2·20	0·93	1·66
11*	4½	42·94	55·82	1·24	2·17	1·12	1·95
12	3¼	44·20	54·61	1·19	2·13	1·14	2·05
13	4	45·12	53·55	1·33	2·43	1·17	2·15
14	3½	44·34	54·41	1·25	2·28	1·23	2·21
15	4	43·70	55·07	1·23	2·18	1·01	1·81
16	4¾	43·06	55·59	1·35	2·39	1·24	2·18
17	4	43·90	54·92	1·18	2·11	1·13	2·03
18	4	42·12	56·65	1·23	2·12	1·23	2·14
19	4¾	42·58	55·99	1·43	2·50	1·34	2·34
20*	4¾	41·06	57·23	1·71	2·90	1·39	2·38
21*	4½	44·07	54·67	1·26	2·26	1·08	1·94
22	4	44·46	54·22	1·32	2·38	1·18	2·14
23	4¾	43·43	55·24	1·33	2·35	1·19	2·10
24*	4½	42·89	55·68	1·43	2·52	1·17	2·05
25*	4	41·34	57·76	0·90	1·54	1·33	2·27
Mean.	4	1085·84	1381·61	32·55	57·57	31·53	55·72
		43·43	55·26	1·30	2·30	1·26	2·22

Lime-water has also been recommended to prevent the transformation of starch during panification into dextrin, sugar, and lactic acid. It was first suggested by Liebig, and is said to have been used to a considerable extent by the Glasgow bakers. Odling finds, from laboratory experiments, that lime-water is quite as effective as alum in preventing the action of diastase upon starch, but seems to have scarcely any influence on the fermentation induced by yeast, or, at any rate, a much less action than alum, which certainly retards the process in a perceptible degree. In this respect then lime-water possesses an advantage over alum; it would also doubtless be considered less objectionable in its direct action on the digestive organs. Bread made with it is of agreeable taste, of rather more porous texture than ordinary baker's bread, and quite free from sourness.

There are doubtless many other mineral substances which would act in the same way as alum or lime-water. Thus **sulphate of copper** acts very powerfully in opposing the action of diastase, and is said to have been used for that purpose in Belgium, an ounce of the salt being dissolved in about a quart of water, and a wine-glassful of this solution mixed with the water necessary for fifty quartern or four-pound loaves. This quantity is extremely small; nevertheless the use of so poisonous a substance as sulphate of copper cannot be too strongly condemned: bread containing copper would be sure to act injuriously in the long run.

Mineral substances added to bread may be detected and estimated in the ash by the ordinary processes of inorganic analysis. A few details may, however, be added relating to the detection and estimation of alumina. The bread taken for examination should be crumb, from the middle of the loaf; it should be carefully trimmed from crust and outside crumb, as those portions may be dirty. It is then to be charred on a platinum tray; the charcoal reduced to powder and incinerated in a muffle (p. 418); the ash digested in pure strong hydrochloric acid; the filtered solution evaporated to dryness to render silica insoluble; the dried residue drenched with strong hydrochloric acid, then boiled with water, and the liquid filtered. The acid filtrate must next be nearly neutralised with carbonate of sodium, pure alcoholic potash added in excess, which will precipitate earthy phosphates and retain alumina in solution, and the liquid boiled and filtered; aqueous potash must not be used, as it always contains alumina. The alkaline filtrate is then to be slightly supersaturated with hydrochloric acid and boiled with carbonate of ammonium; this will precipitate all the alumina, which may then be collected, dried, and tested with nitrate of cobalt before the blowpipe. (See p. 155.)

If a quantitative determination is to be made, it must be remembered that the alumina precipitate generally contains phosphoric acid. To estimate the amount of this acid, the precipitate, after being weighed, is to be dissolved in hydrochloric acid, the solution mixed with tartaric acid, excess of ammonia added (which will produce no precipitate), and then sulphate of magnesium. The phosphoric acid will thereby be precipitated as ammonio-magnesian phosphate, which is converted by ignition into pyrophosphate of magnesium, $Mg^4P^2O^7$, whence the quantity of phosphoric anhydride (P^2O^5) may be calculated, and this, deducted from the total weight of the alumina precipitate, gives the quantity of alumina. Or the precipitated alumina containing phosphate may be dissolved in nitric acid, a piece of metallic tin added, and the liquid boiled: the tin is thereby oxidised, and remains as an insoluble powder, consisting of stannic oxide and phosphate, the whole of the phosphoric acid being thus separated from the alumina. The whole is next evaporated to dryness, the residue treated with water and filtered, and the alumina precipitated from the filtrate by carbonate of ammonia.

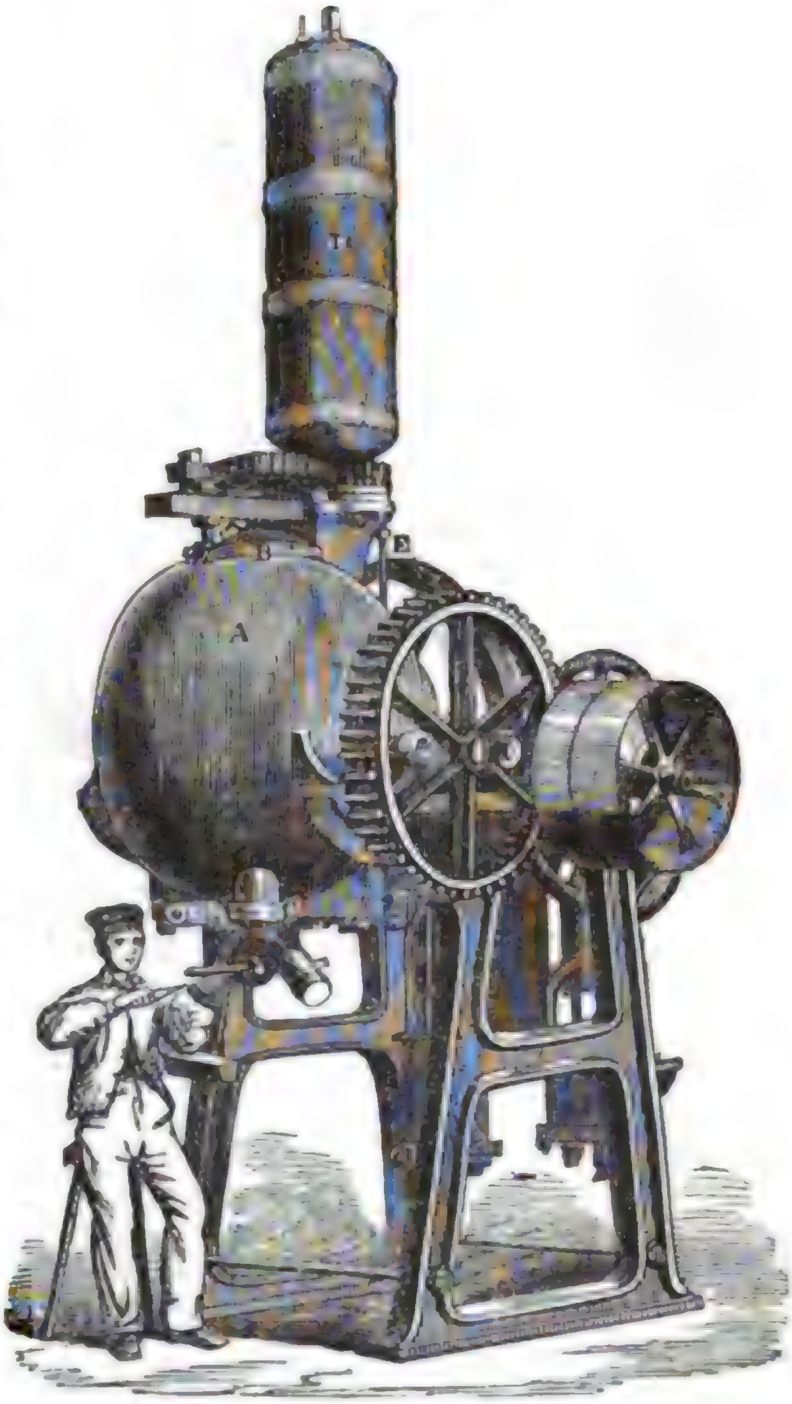
UNFERMENTED BREAD.—Instead of using alum or other mineral substances, as above described, to counteract the injurious secondary actions which take place during the fermentation of dough, methods have been proposed, and to a certain extent carried out, for dispensing with the fermentation altogether, and supplying the carbonic acid which is to give lightness to the dough, from some extraneous source.

1. Instead of mixing salt (chloride of sodium) with the flour and water, hydrochloric acid and carbonate of soda are added in the proportion required to form chloride of sodium, the carbonic acid thereby evolved causing the dough to rise just as if it had been generated by fermentation. Bread thus made is said to be of good quality, though it is never so white as ordinary baker's bread. There is, however, a serious objection to its constant use, namely, that it is liable to be contaminated with arsenic, introduced by the hydrochloric acid. That acid indeed, as found in commerce, always contains arsenic, the complete removal of which can only be effected by a process much too costly and troublesome for the purposes of a bake-house; and though the quantity of arsenic actually present in the bread may be small, still by daily use it might accumulate in the system and ultimately produce injurious effects.

2. *Preparation of* AËRATED BREAD.—Carbonic acid gas produced from chalk, either by the action of dilute sulphuric acid or by ignition, and stored in an ordinary gasholder, is pumped therefrom into a cylindrical vessel containing water, whereby the water becomes charged with the gas. This carbonic acid water is mixed under pressure with the flour, and the resulting dough, which becomes vesicular on the removal of the pressure, is divided into loaves and baked. This process, which was invented and patented by Dr. Dauglish, has been carried out on a large scale in London and other places.

The following is a description of the apparatus:—A (*fig.* 112) is the mixer or vessel in which the flour, water, and salt are mixed together. It consists of a very strong iron spheroïdal vessel, with an internal capacity of from 17 to 20 cubic feet. It has an opening B at the top, to which an air-tight cover is fitted, and the means of closing it to resist considerable pressure. There is also a corresponding opening C at the bottom, large enough for a man-hole, and also closed by a lid, to which is attached the apparatus for drawing off the dough through suitable mouthpieces in a continuous stream, which is cut into pieces by a boy, and received into boxes or baskets to be conveyed to the oven. Through the centre of the mixer, a shaft passes furnished with stuffing boxes, to prevent the escape of compressed gas, and in this shaft suitable mixing arms are fixed: by means of the necessary gearing this shaft is made to rotate by steam power. D is a copper water-vessel, having communication with the mixer from the bottom by means of a valve, and from the top by means of a pipe passing up inside the water-vessel. This water-vessel has also communication with a pair of condensing pumps, which are fixed in the same frame behind the mixer, and are worked by a steam engine. The communication is by means of the pipe E, which terminates within the water-vessel by a rose perforated with minute holes.

Fig. 112.



To work the apparatus, the top cover B of the mixer is opened, and about 560 lbs. of flour are shot into it by means of a hopper and shoot connecting with the floor above; water, to the amount of 30 gallons or so, is drawn into the water-vessel from a cistern above, and the whole is then closed, after adding to the flour the necessary salt. After removing the air from the apparatus by a suitable pump, carbonic acid is pumped by the condensing pump from a gas-holder, in which it is stored until it is condensed to about seven atmospheres. This condensed gas being dispersed by the rose at the bottom of the water-vessel, passes in minute streams through the water, and as the density within increases, the water absorbs the gas in proportion, that which is not absorbed passing down the internal pipe from the top of the water-vessel into the mixer, so that the density within that vessel is kept in equilibrium with that in the water-vessel. When the right density is attained, the valve at the bottom of the water-vessel is opened, when the water falls upon the flour, after which the mixing arms are set to work, and in about six minutes the dough is thoroughly formed. It is allowed to subside for a minute, and is then drawn off through the bottom apparatus, being forced through it by the elastic force of the gas within. On escaping from the condensed atmosphere in the mixer, the dough immediately assumes the vesicular form and texture, and is ready to be baked.

The carbonic acid is obtained by acting on whiting or ground chalk with sulphuric acid; it comes off perfectly pure, and, being kept over water, is thoroughly washed. It takes about 20 cubic feet of carbonic acid at atmospheric density to prepare dough from 280 lbs. of flour, about 11 cubic feet being incorporated with the dough, the remaining 9 cubic feet being wasted in the operation of drawing the dough off, and in other ways: 7 lbs. of sulphuric acid give, in practical working, 21 cubic feet of carbonic acid from 10 lbs. of carbonate of lime, the sulphuric acid being of density of 1·848. The gas which is left in the apparatus after the dough is discharged, is returned to the gas-holder for further use.

The advantages of this process are thus stated by Dr. Odling in a paper read before the Chemical Section of the British Association at Aberdeen in 1859:—1st. Its cleanliness. Instead of the dough being mixed with the naked arms or feet, the bread, from the wetting of the flour to the completion of the baking, is not, and scarcely can be, touched by any one. 2nd. Its rapidity. An hour and a half serves for the entire conversion of a sack of flour into baked loaves; whereas, in the ordinary process, four or five hours are occupied in the formation of the sponge, and a further time in the kneading, raising, and baking of the dough. 3rd. Its preventing the glucogenic deterioration of the flour, which takes place in the ordinary process (p. 657), and thereby obviating the necessity of using alum. 4th. Its certainty and uniformity. Owing to differences in the character and rapidity of the fermentation, dependent on variations of temperature, quality of yeast, &c., the manufacture of fermented bread frequently presents certain vagaries and irregularities from which the new process is entirely free. 5th. The character of the bread. Chemical analysis shows that the flour has undergone less deterioration in bread made by the new than in that made by the fermenting process. In other words, the percentage of extractive matters is smaller. The new bread has been tried dietetically at Guy's Hospital, and by many London physicians, and has been highly approved of. It is well known that, for some years past, the use of fermented bread in dyspeptic cases has been objected to by members of the medical profession, the débris of the yeast being considered unwholesome, and liable to induce acidity. 6th. Its economy. The cost of carbonic acid is alleged to be less than the cost of yeast. Moreover, in making fermented bread, there is a small but necessary waste of the saccharine constituents, which is avoided in the new process. 7th. The saving of labour and health. It substitutes machine labour for manual labour of a very exhausting kind. The sanitary condition of journeymen bakers was investigated some time ago by Dr. Guy, and found to be most lamentable, from their constant night work, and from the fatiguing and unwholesome character of their labour, particularly the kneading. In a politico-economical point of view, the process is also important, as removing bread-making from a domestic manual work to a manufacturing machine work. From the character of the apparatus, the process can only be used profitably on a large scale, and not in small bakeries.

Of all the advantages just noticed, the most important is the prevention of the deterioration of the flour, which is so apt to occur in the ordinary process of bread-making. We have already observed (p. 657) that this deterioration consists in a too great conversion of the starch into dextrin and sugar, and that it takes place to the greatest extent when flour is used which contains the external as well as the central portions of the wheat-grain, because the external portions are rich in nitrogenous matter,—the central consisting almost wholly of starch,—and a portion of this matter passing into a metamorphic state (diastase or cerealin) and acting as a ferment, produces the change just mentioned. Now it is important that this external nitrogenous portion of the grain should be retained—especially for persons who eat but little meat, and to whom bread is essentially the staff of life,—both for its direct nutritive power, and for the part which the metamorphic gluten undoubtedly plays in assisting the solution of the starch and unaltered gluten in the process of digestion. In this country, however, there is an almost universal preference for white bread, and consequently the miller contrives so to grind and dress his flour as to get rid as far as possible of the nitrogenous portion, and thereby prevent the conversion of the starch into dextrin and sugar during fermentation, which, as already observed, is the chief cause of the loss of whiteness. Hence it is, perhaps, as Dr. Dauglish suggests, that wheaten bread has not hitherto entered so extensively into the diet of the poor man in England as oatmeal in Scotland. The latter is prepared for food by simply boiling it in water in the form of a porridge, so that all the elements are presented to the system uninjured by artificial processes, whereas our wheaten bread is generally prepared in such a manner as to rob it of certain of those constituents which not only possess in themselves great nutritive power, but likewise materially facilitate the digestion of the whole. Now the new method of bread-making renders it possible to retain all these matters, and at the same time to produce a light crumbly loaf, without the use of alum or any other mineral ingredient. (See a paper by Dr. Dauglish read before the Society of Arts, 25 April, 1860; also "On Fermented Bread and Aërated Bread," Medical Times and Gazette, 12 May, 1860.)

For further details on the making of bread, and for descriptions and figures of kneading machinery and patent ovens, see the article BREAD in *Ure's Dictionary of Arts, Manufactures, and Mines*, i. 400; *Muspratt's Chemistry*, i. 353; Payen, *Précis de Chimie Industrielle*, 4^{me} éd. ii. 126; *Handwörterbuch d. Chem.* 4^{te} Aufl. ii. [2] 511. On the composition of wheat-grain, flour, and bread, see Lawes and Gilbert. (Chem. Soc. Qu. J. x. 1, 269.)

BREAN. See ICICA RESIN.

BREIDIN and **BREIN.** See ARBOL-A-BREA.

BREISLAKITE. A mineral occurring in cavities of Vesuvian lava, in capillary crystals. Chapman (Phil. Mag. [3] xxxvii. 444) regards it as a variety of augite. The form is that of basaltic augite. Colour brownish or grey with metallic lustre. Melts before the blowpipe to a shining magnetic bead. Not attacked by boiling hydrochloric acid.

BREITHAUPTITE. Native antimonide of nickel, Ni^2Sb (p. 316).

BREMER GREEN. A green pigment consisting chiefly of basic carbonate of copper mixed with alumina and carbonate of calcium. According to Bley, a fine blue-green colour is obtained by dissolving commercial sulphate of copper in 10 pts. of water, adding a little nitric acid, leaving the liquid to itself for a week, then filtering, adding fresh lime-water, precipitating with filtered solution of pearl-ash, and mixing the washed precipitate with gum-water to give it lustre.

BREUNERITE. See MAGNESITE.

BREVICITE. See NATROLITE.

BREWSTERITE. A somewhat rare mineral, occurring in transparent colourless prismatic crystals, of the monoclinic system, with the lateral faces inclined to the terminal faces, at an angle of 93° 40′. Specific gravity 2·12 to 2·2 (Brewster); 2·453 (Mallet). Hardness = 5·0 to 5·5. According to the following analyses by Connell (Ed. N. Phil. J. xiv. 35), Thomson (Mineralogy, i. 348), and Mallet (Sill. Am. J. [2] xxviii. 48), it is of the form $M^2O.Al^4O^3.6SiO^2 + 5H^2O$, the symbol M denoting strontium, barium, and calcium in the atomic proportion Sr : Ba : Ca = 4 : 2 : 1, and by regarding the water as basic and substituting aluminicum ($al = 9·2$) for aluminosum ($Al = 13·7$), the formula may be reduced to $M^2al^6H^{10}Si^6O^{21}$, which is of the form $R^6Si^2O^7$ or $R^4SiO^4.R^2SiO^3$:

SiO^2	Al^4O^3	Ba^2O	Si^2O	Ca^2O	H^2O	Fe^4O^3		
53·67	17·49	6·75	8·32	1·35	12·58	0·29	= 100·45	(Connell)
53·04	16·54	6·02	9·01	0·80	14·73	—	= 100·17	(Thomson)
62·42	15·25	6·80	8·99	1·19	13·22	trace	= 97·87	(Mallet)

Before the blowpipe, it parts with its water and becomes opaque, then froths, and swells up, but melts with difficulty. Leaves a silica skeleton when fused with phosphorus-salt. Dissolves in acids, with separation of silica. It occurs at Strontian in Argyleshire, on the Giant's Causeway, in the lead mines at St. Turpet near Freiburg, in the Breisgau, in the department of Isère in France, and in the Pyrenees.

BREWSTOLIN. A liquid hydrocarbon found in minute cavities in crystals of topaz, chrysoberyl, quartz from Quebec, and amethyst from Siberia, in which it was detected by Sir D. Brewster. It is transparent and colourless, and is nearly thirty-two times as expansible by heat as water, increasing one-fourth of its volume by an increment of 30°, at 50° F. On exposure to the air, it undergoes quick motions and changes, and finally evaporates, leaving a residue of minute solid particles, which, from the moisture of the hand alone, suddenly become fluid again. The residue volatilises by heat, and dissolves in acids without efflorescence. (Dana, ii. 471.)

BRICKS. Common bricks are made with clay mixed with sand or ashes, and baked or burnt at various temperatures. In some southern countries, bricks are merely dried in the sun, but they then remain very friable, and are fit only for light constructions. Nearly all sedimentary or alluvial formations contain clays which may be used for making bricks. Some clays do not require any addition of sand, but with plastic clays an admixture of sand is necessary. In this country, coal-ashes are mixed with the clay, partly to give it the right consistence, partly to facilitate the burning. The clay is dug up and turned over in the winter, and being thus exposed to wet and frost, it breaks up and mixes better with the coal-ashes which are afterwards added. For stiff clays, 50 chaldrons of ashes are added to 240 cubic yards of clay; for clays containing much sand, 40 chaldrons of ashes to 220 cubic yards of clay, and these quantities make 100,000 bricks. The clay and ashes are mixed with water and thoroughly incorporated, first by raking and afterwards in the *pug-mill*, which is an iron-hooped barrel, in the centre of which is a vertical shaft, worked by a horse, and bearing six knives, all of which, except the top one, are furnished with teeth. At the bottom of the barrel, is a small hole, through which the masticated clay is forced by the grinding of the teeth. The clay is next fashioned into bricks in rectangular wooden moulds, previously sanded. The bricks are then dried in the air, and afterwards made up into heaps called *clamps*, having flues or spaces left in them, which are filled with dry wood, on which is put a covering of *breeze*, a coarse kind of coal-ash left from the sifting. The clamp when full is surrounded with old bricks, and on the top of all a thick layer of breeze is laid. The external bricks at the sides are coated with a thin plastering of clay, to exclude the air, and in wet weather protected by hurdles having rushes woven into them. The fire is lighted at the mouths of the flues, which, if it burns well, are then stopped up. In favourable weather, the bricks are burnt in about twenty-five or thirty days. In this mode of burning, the coal-ashes incorporated in the substance of the bricks contribute greatly towards the effect. Sometimes, however, bricks are burned in kilns, and then they have no ashes mixed with them, the firing being wholly external.

Fire-bricks are bricks made of refractory clay, that is of clay which will stand a very strong heat without fusing. Such clays must be free from lime and oxide of iron. The clay of Stourbridge in Worcestershire, and those of Burgundy are celebrated for their fire-resisting qualities, and are therefore used for making bricks for lining furnaces. The clay is mixed with sand or with the fragments of old firebricks ground to powder. (See *Ure's Dictionary of Arts, Manufactures, and Mines*, i. 441.)

BRICKS (FLOATING). Bricks that swim on water were manufactured by the ancients; and Fabbroni discovered some years since, a substance, at Castel del Piano, near Santa Fiora, between Tuscany and the States of the Church, from which similar bricks might be made. It constitutes a brown earthy bed, mixed with the remains of plants. Haüy calls it *talc pulvérulent silicifère*, and Brochant considers it as a variety of *meerschaum*. The Germans name it *Bergmehl* (mountain meal), and the Italians *latte di luna* (moon milk). According to Klaproth's analysis, it consists of 79 silica, 5 alumina, 3 oxide of iron, 12 water, and 1 loss, in 100 pts. It agrees nearly in composition with *Kieselguhr*. U.

BRILLIANT. Diamond cut in such a way as to reflect light most vividly, is called a brilliant. See Diamond.

BRIMSTONE. See Sulphur.

BRINDONIA INDICA. A plant belonging to the order *Guttiferæ*. The pericarp of the fruit is used in Goa as a spice, and the blood-red acid juice as a lemonade. The seeds are convex, red-brown, tasteless, of the size of ordinary beans, and contain 1·72 per cent. nitrogen, or after removal of the fat, 2·58 per cent. In the dry state, they do not yield any fat by pressure, requiring to be previously softened by vapour of water; by the use of solvents, 30 per cent. of fat may be extracted. The crude fat is nearly colourless, melts at 40° C., dissolves sparingly in hot alcohol, and easily saponifies, yielding glycerin, together with oleic and stearic acids, the latter amounting to 50 per cent. From the crude fat, pure stearic is easily obtained by crystallisation and pressing out the mother-liquor. The red-brown cake left after exhausting the fat with ether, contains a fine red colouring matter, soluble in water and alcohol, insoluble in ether and in acids. (J. Bouis and D'Oliveira Pimentel, Compt. rend. xliv. 1355.)

BRITANNIA METAL. An alloy of tin and antimony. (See Tin.)

BRITHYNE. Syn. with Glauberite.—**BRITISH GUM.** See Dextrin.

BRITTLE SILVER ORE. Native sulphide of silver. See Silver.

BROCATELLO. A calcareous stone or marble, composed of fragments of four colours, white, yellow grey, and red.

BROCCOLI. See Brassica.

BROCHANTITE. A basic sulphate of copper, $Cu^2SO^4.6CuHO$, found native, associated with malachite and red copper ore, at Ekatherinenburg in Siberia, and at Rezbanya in Hungary. Small right rhombic prisms of 117°. Emerald-green, transparent, with glassy lustre; harder than calcspar. Specific gravity 3·80—3·87. Melts before the blowpipe, and forms a bead of reduced copper or charcoal.

BRODDBO TANTALITE. See Tantalite.

BROGNIARDITE. A sulphantimonite of lead and silver, $2PbAgS.Sb^2S^3$, from Mexico. It occurs in masses without cleavage. Lustre metallic. Streak greyish-black. It is rapidly attacked by strong nitric acid. An analysis by Damour (Ann. Min. [4] xvi. 227) gave 19·38 per cent. S, 29·95 Sb, 25·03 Ag, 24·74 Pb, 0·54 Cu, and 0·04 Zn.

BROGNIARTIN or **BROGNIARTITE.** Syn. with Glauberite.

BROMACETIC ACID, $C^2H^3BrO^2$.—(W. H. Perkin and B. F. Duppa, Chem. Soc. Qu. J. xi. 22.)

Formation.—By the action of bromine on acetic acid:—

$$C^2H^4O^2 + Br^2 = C^2H^3BrO^2 + HBr.$$

A small quantity of dibromacetic acid is formed at the same time.

Preparation.—A mixture of glacial acetic acid and bromine in equal numbers of atoms (an excess of acetic acid being used to absorb the hydrobromic acid and thereby diminish the pressure) is introduced into a strong sealed tube, and heated in an oil-bath to 150° C., and the bath is then left to cool gradually. When the temperature has fallen to about 146°, the mixture suddenly becomes nearly colourless, or light amber-brown, and at the same time, the tubes are apt to burst, though the temperature of the bath may have risen as high as 155°. The tube when quite cold is opened, torrents of hydrobromic acid gas then escaping; the contents are transferred to a retort provided with proper apparatus for condensing the hydrobromic acid, and heated to 200°; and the retort is left to cool. The whole contents then solidify after a while into a beautifully crystalline mass, consisting of bromacetic and dibromacetic acids, mixed with a little hydrobromic acid, to remove which the mixture is heated to 130°, and carbonic acid gas passed through it till the presence of hydrobromic acid is no longer indicated by nitrate of silver. Carbonate of lead is then added in excess, together with a volume of water about ten times as great as that of the acid; and the whole is heated to 100°, and allowed to stand for some hours. Bromacetate of lead then crystallises out, while dibromacetate remains in solution. The crystals may be freed from the last portions of this salt by washing with a little cold water. Lastly, the crystals of bromacetate of lead are suspended in water and decomposed by sulphuretted hydrogen, and the filtered liquid is evaporated till it crystallises.

Bromacetic acid forms rhombohedral crystals which are very deliquescent. It melts below 100° C., and boils at 208°; attacks the skin powerfully, raising a blister like a burn; when the acid is dilute, this effect takes place after eight or ten hours only. It is very soluble in water.

The acid strongly heated in a sealed tube, is resolved into dibromacetic acid, carbonic oxide, and apparently marsh-gas, together with water and hydrobromic acid, probably as represented by the equation:

$$3C^2H^3BrO^2 = C^2H^2Br^2O^2 + 3CO + CH^4 + HBr + H^2O.$$

On distilling it with acetate of potassium, acetic acid is evolved.—Heated with metallic zinc, it yields acetate and bromide of zinc.—Heated with ammonia, it forms bromide of ammonium and glycocine:

$$C^2H^3BrO^2 + 2NH^3 = NH^4Br + C^2H^5NO^2.$$

The acid is monobasic, the formula of its salts being $C^2H^2BrO^2.M$. Most of them are crystallisable and many of them decompose rapidly.

Bromacetate of Ammonium.—Nearly uncrystallisable; very soluble in water; decomposes when heated, yielding bromide of ammonium.

Bromacetate of Barium crystallises with difficulty in small stars containing water of crystallisation; it is tolerably soluble in alcohol.

Bromacetate of Calcium is a very difficultly crystallisable salt, very soluble in water.

Bromacetate of Copper is a green crystalline salt, very soluble in water. A solution of it appears to decompose when boiled, as the colour becomes paler. The solution, after standing for some days, deposits needle-shaped crystals and small malachite-green tufts of great beauty, which appear to contain a large quantity of water of crystallisation.

Bromacetate of Lead.—Obtained, either by neutralising bromacetic acid with oxide of lead and recrystallising the product from water; or by adding a solution of bromacetic acid to a solution of acetate of lead, washing the resulting crystalline precipitate with cold water, and recrystallising from water. Crystallises in needles, sparingly soluble in cold, but moderately soluble in hot water.

Bromacetate of Potassium.—Obtained by neutralising a solution of carbonate or hydrate of potassium with bromacetic acid, and evaporating the solution in a water-bath. It is a crystalline salt, very soluble in water and alcohol.

Bromacetate of Silver. $C^2H^2BrAgO^2$.—Obtained by treating bromacetic acid with carbonate of silver, or by adding a solution of bromacetic acid to a solution of nitrate of silver. In the latter case, it is thrown down as a beautiful crystalline precipitate, which may be washed with cold water, and dried over sulphuric acid in vacuo. Contains 43·62 per cent. silver (by calculation, 43·9). It is very unstable. The dry salt heated to about 90° C., decomposes with a sort of an explosion. It is rapidly acted upon by light when moist. Boiled with water, it yields bromide of silver and glycollic acid:

$$C^2H^2BrAgO^2 + H^2O = AgBr + C^2H^4O^3.$$

Bromacetate of Sodium is very soluble in water, but insoluble, or nearly so, in alcohol.

BROMACETIC ETHERS.—*Bromacetate of Methyl,* $C^3H^5BrO^2 = C^2H^2BrO^2.CH^3$, is obtained by heating amixture of methylic alcohol and bromacetic acid in a sealed tube for an hour, to a temperature of 100° C., washing the product with water, drying over chloride of calcium, and rectifying. It is a transparent, colourless, mobile liquid, having an aromatic odour highly irritating to the nose and eyes. It is heavier than water; boils at about 144° C., decomposing gradually every time it is distilled. Ammonia acts on it very readily.

Bromacetate of Ethyl. $C^4H^7BrO^2 = C^2H^2BrO^2.C^2H^5$.—Obtained in a similar manner to the preceding. It is a clear colourless liquid, heavier than water, and highly irritating to the eyes and nose. It boils at 159° C. Decomposes partially every time it is distilled, with evolution of hydrobromic acid. It is rapidly acted on by ammonia.

Bromacetate of Amyl. $C^7H^{13}BrO^2 = C^2H^2BrO^2.C^5H^{11}$.—Obtained by heating amylic alcohol with excess of bromacetic acid, washing the product with water, and drying over chloride of calcium. It is an oily liquid which has a pleasant odour when cold, but if heated, acts upon the eyes and nose like the preceding. It boils at 207° C., and decomposes partially every time it is distilled. Ammonia acts but slowly upon it in the cold.

The bromacetates of methyl, ethyl, and amyl, boil at temperatures about 82° to 86°C. higher than the acetates. Thus—

	Boiling-point.		Boiling-point.	Diff.
Bromacetate of Methyl .	144° C.	Acetate of Methyl .	58° C.	86°
„ Ethyl .	159°	„ Ethyl .	74°	85°
„ Amyl .	207°	„ Amyl .	125°	82°

A similar difference exists between the boiling points of bromacetic acid (208°), and acetic acid (120°).

Dibromacetic Acid. $C^2H^2Br^2O^2$. (Perkin and Duppa, Chem. Soc. Qu. J. xii. 1.)—Formed, together with monobromacetic acid, when a mixture of bromine and acetic acid is exposed to light (p. 663). To obtain it in quantity, the monobrominated acid is exposed to the action of bromine-vapour in strong sunshine. The product may be freed from hydrobromic acid by passing a stream of dry carbonic acid gas through it at 120° C.

It is a colourless, inodorous liquid, of specific gravity 2·25; it was once, during very cold weather, obtained in fine needle-shaped crystals. When placed on the skin, it produces painful blisters like burns. It boils between 225° and 230° C., but cannot be distilled without decomposition. It dissolves readily in water, producing cold; also in alcohol and ether. Zinc decomposes it, with evolution of hydrogen.

Dibromacetate of Ammonium. $C^2H^2Br^2O^2.NH^4 + \frac{1}{2}aq.$—Obtained by neutralising the acid with dilute ammonia and leaving the solution to evaporate, either in the air or over sulphuric acid in vacuo. Forms splendid crystals, which give off their water at 100°, becoming white and opaque. Heated to 100° C. with excess of ammonia, it is decomposed, giving off volatile products, which have not yet been examined. It dissolves readily in water, alcohol, and ether.

Dibromacetate of Potassium is a beautifully crystalline salt, shooting out into long and very brilliant crystals, containing water of crystallisation; very soluble in alcohol and water, but not deliquescent.

Dibromacetate of Lead is a very soluble and uncrystallisable substance, drying up to a tough gum-like mass. When added to water in excess, it fuses and runs about like a heavy oil; it is formed by adding the acetate or carbonate of lead to dibromacetic acid.

Mercurous Dibromacetate is precipitated on adding a solution of mercurous nitrate to dibromacetic acid; it much resembles dibromacetate of silver, and like it undergoes decomposition when boiled.

Dibromacetate of Silver is formed by adding the carbonate or nitrate of silver to dibromacetic acid; it crystallises in small needles, often grouped in stars when the acid is dilute. It is easily decomposed at 100° C. yielding bromide of silver and bromoglycollic acid:

$$\underset{\substack{\text{Dibromacetate}\\ \text{of silver.}}}{C^2HBr^2O.Ag.O} + H^2O = \underset{\substack{\text{Bromoglycollic}\\ \text{acid.}}}{C^2HBrO.H^2.O^2} + AgBr.$$

Dibromacetic acid heated with *ethylic* and *amylic alcohols*, yields the corresponding ethers. The ethyl-compound is decomposed by ammonia, yielding alcohol and dibromacetamide:

$$C^2HBr^2.C^2H^5.O^2 + NH^3 = C^2H^5.H.O + N.H^2.C^2HBr^2O.$$

BROMACETINS. See Acetins.

BROMAL. *Hydride of Tribromacetyl. Oxide de Bromèthile.* $C^2HBr^3O = C^2Br^3O.H.$ (Löwig, Ann. Ch. Pharm. iii. 228.)—A compound analogous to chloral, and produced in like manner, by the action of bromine on alcohol. 3 or 4 pts. by weight of bromine are gradually added to 1 pt. of absolute alcohol, cooled by ice; the mixture is left to itself for ten or twelve days, and then distilled; and after three-fourths (consisting of hydrobromic acid, bromide of ethyl, and other products) have passed over, the residue is mixed with water, and exposed to the air for a day or more in a shallow basin. It then deposits large crystals of hydrate of bromal, which yield the anhydrous compound by distillation with sulphuric acid. Or they may be gently heated with six times their weight of strong sulphuric acid, and the anhydrous bromal, which then sinks to the bottom as a colourless oil, may be separated by decantation and distilled, first over slaked and then over quick lime.

Bromal is said to be also produced by the action of bromine on a mixture of alcohol and nitric acid. (Aimé.)

Bromal is a transparent colourless oil, of specific gravity 3·34. It is somewhat greasy to the touch, and makes grease-spots upon paper, which however soon disappear. Its boiling point is above 100° C. and it may be distilled without decomposition. It has a peculiar pungent odour, and excites a copious flow of tears. Its taste is extremely sharp and burning, and very persistent.

Bromal is decomposed by aqueous alkalis in the same manner as chloral, yielding bromoform, $CHBr^3$, and a formate of the alkali-metal. Lime and baryta heated in its vapour become incandescent, and decompose it, yielding carbonic oxide, water, and a bromide of the metal mixed with charcoal. Red-hot iron acts in a similar manner. It is not decomposed by nitric acid, sulphuric acid, or chlorine.

Hydrate of Bromal. $C^2HBr^3O.2H^2O$.—Bromal dissolves in a small quantity of water, and the solution, when left to evaporate, yields the hydrate in large crystals, having the form of sulphate of copper. They melt at the heat of the hand, dissolve readily in water, and yield anhydrous bromal when treated with sulphuric acid. The hydrate is also formed when bromal is exposed to moist air.

Bromal dissolves sulphur and phosphorus, and mixes readily with bromine, also with alcohol and ether.

BROMALOÏN. See Aloin (p. 148).

BROMAMIDE. See Nitrogen, Bromide of.

BROMANIL. Syn. of Perbromoquinone. See Quinone.

BROMANILAMIC ACID. BROMANILIC ACID. BROMANILAMIDE. Syn. with Dibromoquinonamic Acid, Dibromoquinonic Acid, and Dibromoquinonamide. (See Quinonic Acid.)

BROMANILOIDE. See Tribromophenylamine, under Phenylamine.

BROMANISIC ACID. See Anisic Acid.—**BROMANISOL.** See Anisol.

BROMARGYRITE. Native bromide of silver. (See Silver.)

BROMEIN. $C^{10}H^6Br^4$?—A crystalline product, obtained in small quantity by the action of bromine on crude benzene. (Laurent.)

BROMETHERIDE, BROMETHERIN, BROMETHEROIDE. See Vinyl, Bromide of.

BROMETHIONESSIL. A product of the action of bromine on thionessal (*q. v.*) It forms colourless tables, apparently consisting of $C^{28}H^{14}Br^4S$. (Laurent.)

BROMHYDRIC ACID. See Bromide of Hydrogen.

BROMHYDRINS. (Berthelot and De Luca, Ann. Ch Phys. [3] xlviii. 304; lii. 433.)—These compounds are produced by the action of tribromide or pentabromide of phosphorus on glycerin. Their composition is such as might result from the combination of glycerin and hydrobromic acid, with elimination of water, and may be represented empirically by the general formula

$$m\,C^3H^8O^3 + n\,HBr - p\,H^2O.$$

Their names and formulæ are as follows:

Monobromhydrin . .	$C^3H^7BrO^2 = C^3H^8O^3 + HBr - H^2O$
Epibromhydrin . .	$C^3H^5BrO = C^3H^8O^3 + HBr - 2H^2O$
Dibromhydrin . .	$C^3H^6Br^2O = C^3H^8O^3 + 2HBr - 2H^2O$
Tribromhydrin . .	$C^3H^5Br^3 = C^3H^8O^3 + 3HBr - 3H^2O$
Hemibromhydrin . .	$C^6H^9BrO^2 = 2C^3H^8O^3 + HBr - 4H^2O$
Hexaglyceric Bromhydrin	$C^{18}H^{27}BrO^7 = 6C^3H^8O^3 + HBr - 11H^2O$

Mono-, di-, and tribromhydrin, may also be regarded as glycerin, $C^3H^5(HO)^3$, in which 1 or more at. of peroxide of hydrogen has been replaced by bromine.

Besides these compounds, there are formed at the same time others of similar nature, which have not been examined; likewise acrolein, and dibromallylphosphine, $C^6H^9Br^2P = P.H^2.(C^3H^4Br)^2$.

The bromhydrins heated with aqueous potash to 100° C., in closed vessels, all yield bromide of potassium and glycerin.

Preparation of the Bromhydrins.—500 grms. of glycerin are added by small portions to between 500 and 600 grms. of liquid bromide of phosphorus, the liquid being cooled after each addition, and the mixture, after standing for twenty-four hours, is distilled into a well-cooled receiver communicating with a vessel containing potash-ley, to absorb the acrolein vapour. As an additional precaution against the injurious effects of this vapour, the distillation and all the subsequent operations should be performed either in the open air, or under a chimney with a good draught.

The distillate, consisting of an upper watery layer and a lower liquid insoluble in water, may be freed from part of the acrolein by heating it in the water-bath. It is then mixed with potash in sufficient quantity to supersaturate the acid and destroy the acrolein, and the watery layer is separated from the lower liquid.

The watery liquid is then treated with ether, whereby an ethereal solution is obtained, which, when quickly evaporated, leaves a residue chiefly consisting of the most volatile products of the reaction, together with *epibromhydrin.* The lower liquid, which is insoluble in water and requires to be treated for several hours with sticks of potash, consists chiefly of *epibromhydrin* and *dibromhydrin.* The residue which remains in the retort after the distillation, is suspended in water, supersaturated with carbonate of potassium, and shaken up with ether, and the filtered etheral extracts are evaporated: they then leave a mixture of *dibromhydrin, monobromhydrin,* and several other substances.

To separate the individual substances contained in these several mixtures, the mixtures are subjected to repeated fractional distillation, and the portion which does not volatilise at 240° C. under the ordinary atmospheric pressure, is fractionally distilled under diminished pressure (about 10mm. of mercury). The distillate thus obtained between 120° and 160° consists chiefly of dibromhydrin; between 160° and 200°, the compound $C^6H^9Br^2P$ passes over together with monobromhydrin, and between 200° and 300°, syrupy liquids which cannot be further separated, but appear to be bromhydrins. In the retort there remains a thick syrup, together with a black crystalline compound which is *hexaglyceric bromhydrin.*

Monobromhydrin, $C^3H^7BrO^2 = (C^3H^5)'''.(HO)^2.Br$.—This compound, which passes over at 180° C. in the distillation under diminished pressure, is a neutral oily liquid, soluble in ether, and having a sharp aromatic taste.

Dibromhydrin, $C^3H^6Br^2O = (C^3H^5)'''.HO.Br^2$.—This, which is the chief product of the action, is a neutral liquid, of specific gravity 2·11 at 18° C. boiling at 219°, having an ethereal odour, and soluble in ether. Heated with pentabromide of phosphorus, it yields tribromhydrin. Heated to 140° with metallic tin, it is decomposed, yielding bromide of tin and a tin-compound insoluble in water but soluble in ether.

When gaseous ammonia is passed into pure dibromhydrin, the liquid becomes hot, and yields bromide of ammonium, together with an amorphous substance, $C^6H^{12}BrNO^2$, insoluble in water, ether, alcohol, and acetic acid:

$$2C^3H^6Br^2O + 4NH^3 = 3NH^4Br + C^6H^{12}BrNO^2;$$

but if the ammonia gas is passed into a solution of dibromhydrin in absolute alcohol, the products formed are bromide of ammonium and *hydrobromate of glyceramine:*

$$C^3H^6Br^2O + (NH^4)^2O = NH^4Br + C^3H^9NO^2.HBr.$$

Tribromhydrin. $C^3H^5Br^3$.—Obtained by distilling dibromhydrin or epibromhydrin with pentabromide of phosphorus, treating the product with water, distilling, and collecting apart that which passes over between 175° and 180° C. It is a heavy liquid, which fumes slightly in the air, is gradually decomposed by water, and when treated with moist oxide of silver, yields bromide of silver and glycerin. It is isomeric with Wurtz's *tribromide of allyl* (called by Berthelot and De Luca, *isotribromhydrin*), and with *dibromide of bromotritylene,* $C^3H^5Br.Br^2$.

Epibromhydrin or *Oxybromide of Glyceryl.* C^3H^5BrO.—This compound is produced in considerable quantity by the action of the bromides of phosphorus on glycerin. It may be isolated by repeated fractional distillation, the portions which boil at or near 138° C. being each time collected apart. It is a mobile neutral liquid, soluble in ether, with an ethereal odour and pungent taste. Specific gravity 1·615 at 14° C. Boils at 138°. Vapour-density, by experiment, 5·78. (This is considerably above the calculated value, 4·80, probably because the density was taken at a temperature too near the boiling point, viz. at 178°, the compound decomposing rapidly at higher temperatures.)

This compound may be considered as deriving from tribromhydrin, by the substitution of O for Br^2. It is isomeric with *bromide of propionyl,* $C^3H^5O.Br$. Its formula is also that of monobromhydrin *minus* H^2O, or of dibromhydrin *minus* HBr.

Epibromhybrin, heated with aqueous potash to 100° for 112 hours, saponifies, yielding bromide of potassium, glycerin, and a trace of matter soluble in ether. Moist oxide of silver decomposes it rapidly at 100°, forming bromide of silver and glycerrin. Distilled with pentabromide of phosphorus, it is partly converted into tribromhydrin, according to the equation:

$$C^3H^5BrO + PBr^3Br^2 = PBr^3O + C^3H^5Br^3,$$

while the rest undergoes more complete decomposition, yielding a black substance and a gaseous mixture, containing, in 100 volumes, 5·5 carbonic anhydride, 5·5 tritylene, 11·0 hydrogen, and 78·0 carbonic oxide.

Hexaglyceric Bromhydrin. $C^{18}H^{27}BrO^7$.—This compound remains in the retort in the form of a black crystalline mass, impregnated with a syrupy liquid. It is purified by washing with cold ether; boiling ether dissolves it slightly.

Hemibromhydrin. $C^6H^9BrO^2$.—This compound passes over in the fractional distillation between epibromhydrin and dibromhydrin, viz. at 200° C. It is a neutral liquid, soluble in ether, and saponifiable by potash, yielding bromide of potassium, a substance analogous to or identical with glycerin, and a trace of matter soluble in ether. The analyses of the compound are said to agree nearly with the above formula (no analyses are given in Berthelot and De Luca's memoir), according to which it may be regarded as derived from epibromhydrin, in the same manner as the latter from dibromhydrin, viz. by abstraction of half the hydrobromic acid:

$$C^3H^6Br^2O - HBr = C^3H^5BrO:$$

and

$$2C^3H^5BrO - HBr = C^6H^9BrO^2.$$

It is analogous in composition to iodhydrin.

BROMIC ACID. $HBrO^3$ or $H^2O.Br^2O^5$.—This acid is produced: 1. By the action of bromine on alkalis or alkaline earths:

$$6Br + 3K^2O = KBrO^3 + 5KBr.$$

The bromate is separated from the bromide by its inferior solubility. A similar reaction takes place with trioxide of gold, the products being bromate and bromide of gold:

$$18Br + 3Au^2O^3 = \left.\begin{matrix}(BrO^2)^3\\ Au'''\end{matrix}\right\}O^3 + 5AuBr^3.$$

2. In the decomposition of pentachloride of bromine by water or by alkalis:

$$BrCl^5 + 3H^2O = HBrO^3 + 5HCl.$$

To obtain the free acid (bromate of hydrogen) the barium-salt is decomposed with an exactly equivalent quantity of dilute sulphuric acid, and the filtrate concentrated by evaporation at a gentle heat. It cannot, however, be reduced to a syrupy consistence without decomposition. The solution is colourless, acid to the taste, reddens litmus, and then bleaches it. It is decomposed at 100° C., giving off bromine and oxygen. All reducing agents decompose it with facility. With *sulphurous acid* the products are bromine and sulphuric acid; with *sulphydric acid*, water, bromine, and sulphur; with *hydriodic acid*, water and bromide of iodine; with *hydrochloric acid*, water and chloride of bromine; with *hydrobromic acid*, water and bromine, *e.g.*:

$$HBrO^3 + 5HCl = 3H^2O + BrCl^5.$$

Alcohol and *ether* decompose bromic acid, with formation of acetic acid and great rise of temperature.

Bromic acid is monobasic, the formula of the BROMATES being $MBrO^3$ or $M^2O.Br^2O^5$. Most of these salts are soluble in water, though less so than the bromides. They may be prepared by the action of bromic acid on the oxides or carbonates of the metals, or by precipitating bromate of barium with the corresponding sulphates; the bromates of the alkali-metals also by treating the solutions of the alkalis with bromine-water or pentachloride of bromine, and crystallising out the sparingly soluble bromate from the bromide or chloride formed at the same time:

$$\begin{aligned}6KHO + Br^6 &= KBrO^3 + 3H^2O + 5KBr\\ 6KHO + BrCl^5 &= KBrO^3 + 3H^2O + 5KCl.\end{aligned}$$

Bromates are for the most part crystallisable, but many of them decompose when their solutions are heated; hence it is generally best to evaporate the solutions in vacuo or over oil of vitriol. The bromates of mercurosum, silver, and lead are insoluble.

Bromates heated to redness either give off their oxygen and leave bromides (K, Na, Hg, Ag), or they give off bromine and part of their oxygen, and leave oxides, *e.g.*:

$$2ZnBrO^3 = Br^2 + O^5 + Zn^2O.$$

Mixed with charcoal, sulphur, or other combustible substances, they explode by heat or by percussion. Solid bromates heated with *sulphuric acid*, give off bromine and oxygen. A solution of a bromate is coloured red, even by dilute sulphuric acid. By *sulphurous acid* and other reducing agents, they are decomposed in the same manner as the acid. A solution of a bromate, not too dilute, gives with *lead-salts*, a white precipitate; with *mercurous salts*, a yellowish white precipitate, insoluble in cold nitric acid; and with *silver-salts*, a white precipitate almost insoluble in water, sparingly soluble in nitric acid, easily in ammonia. This precipitate is distinguished from chloride of silver by giving off red vapours of bromine when heated with sulphuric acid. The reactions with silver-salts and with sulphuric acid distinguish bromates from chlorates (*q.v.*)

Bromate of Aluminium.—Obtained as a clear, viscid, deliquescent mass, by dissolving hydrate of aluminium in bromic acid, or by precipitating bromate of potassium with silicofluoride of aluminium, and evaporating the filtrate over sulphuric acid.

Bromate of Ammonium. NH^4BrO^3.—White needles or crystalline granules, apparently belonging to the regular system. It cannot be preserved in the solid state, as it decomposes after a while, with violent detonation, even at ordinary temperatures, yielding nitrogen, bromine, oxygen, and water. Hydrochloric acid decomposes it, forming, however, but a small quantity of chloride of ammonium.

Bromate of Barium. $2BaBrO^3 + aq.$—When bromine or chloride of bromine is added to baryta-water till the colour begins to be permanent, bromate of barium crystallises out, while bromide or chloride remains in solution. But a better mode of preparation is to decompose 100 pts. bromate of potassium dissolved in boiling water, with 74 pts. crystallised chloride or 78 pts. anhydrous acetate of barium, and leave the liquid to cool slowly; the bromate of barium then separates out, while chloride or acetate of potassium remains in solution. Acetate of barium is preferable to the chloride for this preparation, on account of the greater solubility of the acetate of potassium.

Bromate of barium forms a crystalline powder or thin prisms of the monoclinic system, with the faces $\infty P . \infty P\infty . (\infty P\infty) . P\infty . oP . +P\infty . -\infty P$. Inclination of faces, $\infty P : \infty P = 82° 10'$; $(P\infty) : (P\infty) = 79° 5'$; $oP : \infty P\infty = 93° 2'$; $\infty P\infty : P\infty = 138°$. The salt is isodimorphous with chlorate of barium (Rammelsberg. Pogg. Ann. xc. 16). It dissolves in 130 pts. of cold and 24 pts. boiling water. It does not give off its water of crystallisation till heated above 200° C. When thrown on red-hot coals, it detonates with a green light. When heated alone, it is resolved, with evolution of light and heat, into bromide of barium and oxygen gas, without forming a perbromate. Hydrochloric or moderately dilute sulphuric acid decomposes it with separation of chloride of bromine or free bromine; very dilute sulphuric acid separates undecomposed bromic acid.

Bromate of Bismuth.—When bromic acid is poured upon hydrate of bismuth, a basic insoluble salt is formed, together with a small quantity of dissolved salt. The basic salt, $3Bi^2O^3.2Br^2O^5 + 6 aq.$, is a white amorphous powder.

Bromate of Cadmium. $2CdBrO^3 + aq.$—Rhombic prisms of 127° and 53°, with four-sided summits and truncation of the acute lateral edges by two narrow faces. Soluble in 0·8 pts. cold water. Decomposed by heat, leaving oxide of cadmium mixed with bromide.

Ammonio-bromide of Cadmium, $3NH^3.CdBrO^3$, is deposited from an ammoniacal solution of bromide of cadmium evaporated over quick lime, as a white crystalline powder, which gives off ammonia when heated, and is decomposed by water.

Bromate of Calcium. $2CaBrO^3 + aq.$—Monoclinic tables or needle-shaped prisms; $\infty P : \infty P$ in the clino-diagonal section $= 79° 56'$; $\infty P2 : \infty P2$ in the same $= 118° 22'$; $+P : +P$ in the same $= 98° 41'$: $-P : -P$ in the same $= 106° 22'$: $(\frac{1}{2}P\infty) : (\frac{1}{2}P\infty)$ in the same $= 123° 33'$ (Rammelsberg). Dissolves at mean temperature in 1·1 pt. water, forming a syrupy solution. The crystals gives off their water at 180° C.; at a stronger heat, oxygen is given off and bromide of calcium remains.

Bromate of Cerium. $2CeBrO^3 + aq.$—Colourless laminæ, which dissolve easily in water, and do not effloresce over sulphuric acid.

Bromate of Chromium.—Chromic sulphate decomposed by bromate of barium yields a green filtrate, which decomposes by evaporation, giving off bromine and leaving a dark red residue, consisting almost wholly of chromic acid.

Bromate of Cobalt. $CoBrO^2 + 3 aq.$—Hyacinth-red, transparent octahedrons, soluble in 2·2 pts. water; the solution is decomposed by heat. The dry salt when heated leaves a residue of oxide of cobalt. The salt dissolves in aqueous ammonia, forming a red liquid which turns brown in the air, and yields, after filtration, dark-brown crystals, probably consisting of the bromate of Fremy's *fuscocobaltia*.

Bromate of Copper, $2CuBrO^3 + 5 aq.$, crystallises from a concentrated solution in light-blue or blue-green crystals, which are very soluble in water, do not effloresce in the air, but crumble to a greenish-white powder in vacuo over sulphuric acid. They retain a small portion of their water even at 180° C., but give it off at 200°, together with part of the bromine. The aqueous solution mixed with a little ammonia yields a light-blue precipitate, consisting of a basic salt, $6Cu^2O.Br^2O^5 + 10$ aq., which at 200° gives off its water and becomes greyish-green.

Ammonio-bromate of Copper, $2NH^3.CuBrO^3$, separates as a dark-blue crystalline powder on adding alcohol to a solution of bromate of copper in excess of ammonia. It dissolves in a small quantity of water, and is decomposed by excess of water, with separation of a basic salt. When heated it decomposes with deflagration.

Bromates of Iron.—A solution of ferric hydrate in bromic acid, yields by evaporation over sulphuric acid, a syrup, which, after drying over the water-bath, leaves a nearly pure basic salt, $5Fe^4O^6.Br^2O^5 + 30$ aq., insoluble in water.

A solution of ferrous carbonate in bromic acid yields by evaporation in vacuo, octahedral crystals of *neutral ferrous bromate*, $FeBrO^3$, the solution of which easily decomposes, with separation of the basic ferric salt.

Bromate of Lanthanum. $LaBrO^3 + 3$ aq. — Amethyst-coloured crystals (? containing didymium), which give off 20 per cent. water at 160° C.

Bromate of Lead. $2PbBrO^3 +$ aq.—Obtained by precipitation, or better by dissolving carbonate of lead in warm bromic acid; it then crystallises on cooling in small shining prisms, isomorphous with the strontium salt. The crystals are permanent in the air, and do not give off any water over sulphuric acid; they dissolve in 75 pts. water at mean temperature. The salt begins to give off oxygen and bromine at 180° C., a small quantity of brown peroxide of lead being formed at the same time, whereas at a stronger heat, red lead or the yellow protoxide is formed; the residue contains protoxide with a small quantity of bromide.

Bromate of Lithium, $LiBrO^3$, crystallises from a syrupy solution over sulphuric acid, in needles, which effloresce in a dry atmosphere, but deliquesce when exposed to the open air.

Bromate of Magnesium. $MgBrO^3 + 3$ aq. — Large regular octahedrons, which dissolve in 1·4 pts. water at 15° C.; melt in their water of crystallisation at a moderate heat, give off the greater part of it at 200° C.; and the last portion at a somewhat higher temperature, oxygen being at the same time evolved.

Bromate of Manganese is formed by dissolving manganous oxide in bromic acid, but decomposes very quickly.

Bromates of Mercury. — *The mercuric salt*, $HgBrO^3 +$ aq., is obtained by pouring bromic acid on recently precipitated mercuric oxide, as a white powder, which dissolves in 600 pts. of cold and 64 pts. boiling water. It dissolves also in excess of warm bromic acid, and crystallises in small prisms on cooling. Hydrochloric acid dissolves it with decomposition. At 130° — 140° C. it decomposes with detonation, yielding a sublimate of mercurous and mercuric bromide, and a residue of mercuric oxide; but giving off part of the bromine and oxygen as gas. Ammonia added to the warm aqueous solution throws down a compound of mercuric bromate with oxide of dimercurammonium, $2HgBrO^3.(NH^2Hg^2)^2O$, which does not yield any ammonia when treated with potash. It is decomposed by heat with violent detonation.

Mercurous bromate, Hg^2BrO^3 or $HhgBrO^3$, is obtained as a white powder by precipitation, or by completely saturating bromic acid with mercurous oxide. From a solution of the oxide in a slight excess of bromic acid, it separates by evaporation in shining crystalline laminæ. Water decomposes it, forming a basic salt, $Hhg^2O.2HhgBrO^3$. It decomposes with detonation when heated.

Bromate of Nickel. $NiBrO^3 + 3$aq. — Green regular octahedrons having their summits replaced by cube-faces. Thin plates cut parallel to the cube-faces act strongly on polarised light (Marbach, Pogg. Ann. xciv. 412). The salt gives off water when heated. It dissolves in 3·6 pts. of cold water, also in ammonia, and on adding alcohol to the ammoniacal solution, a blue-green powder is precipitated, consisting of *ammonio-bromate of nickel*, $NH^3.NiBrO^3$, or *bromate of nickel-ammonium* $(NH^3Ni)BrO^3$.

Bromate of Palladium appears to be produced by dissolving palladous hydrate in bromic acid.

Bromate of Platinum.—Platinic sulphate decomposed by bromate of barium yields a yellow filtrate, which, when evaporated, gives off oxygen and bromine-vapour, and deposits platinic bromide.

Bromate of Potassium. $KBrO^3$. — Prepared by adding bromine to a warm, moderately concentrated solution of potash, till the liquid acquires a permanent yellowish tint; the salt then separates almost completely on cooling, and may be purified from bromide of potassium by washing with water, and recrystallisation. It forms colourless anhydrous crystals of specific gravity 3·271 (Kremers). From a hot solution it crystallises in needles, but by slow cooling it is obtained in four- and six-sided plates, or in cubes with rounded summits; by spontaneous evaporation in small scales, or sometimes in dendritic masses. According to Fritzsche, it always crystallises in forms of the regular system; but, according to Rammelsberg, in rhombohedrons, having the angles of the terminal edges = 86° 18′, and in forms derived therefrom. It dissolves in 32·1 pts. water at 0° C., in 18·5 pts. at 10°, in 14·4 pts. at 20°, in 7·5 pts. at 40°, in 4·4 pts. at 60°, in 2·9 pts. at 80°, and in 2 pts. at 100° (Kremers, Pogg. Ann. xcii. 497; xciv. 255; xcvii. 1; xcix. 25, 58). According to Pohl, 1 pt. of the salt dissolves in 17·5 pts. water at 17° C. The crystals deposited from a solution, either perfectly neutral or slightly acidulated with acetic acid, decrepitate with violence at 300°—350° C., and crumble to a powder, which, if thrown into water, gives off bubbles of pure oxygen gas as it dissolves; but the solution when evaporated yields nothing but pure bromate of potassium, probably reproduced by absorption of oxygen from the air. The crystals deposited from an alkaline solution decrepitate but slightly when heated, and the powder dissolves in water without perceptible evolution of gas. (Fritzsche, J. pr. Ch. xxiv. 285.)

Bromate of potassium is decomposed by strong sulphuric acid, with violent decrepitation and evolution of bromine and oxygen. When heated *per se*, it melts at a temperature above 350° C., and then decomposes, with evolution of oxygen, slowly at first, but afterwards with explosive violence, beginning to glow at one point, and then quickly becoming incandescent through the entire mass. When mixed with combustible bodies, it explodes with great violence when struck or heated.

Bromate of Silver. $AgBrO^3$.—Obtained by precipitation as an amorphous white powder quickly turning grey when exposed to light. According to Rammelsberg, it forms shining quadratic prisms (P : P in the terminal edges = 121° 58·7, in the lateral edges = 86° 38), isomorphous with chlorate of silver. When rapidly heated, it explodes with deflagration, giving off part of the bromine in the form of yellow vapour. It dissolves sparingly in water and in nitric acid, more easily in ammonia, the solution yielding by spontaneous evaporation, colourless prisms, which are quickly decomposed by water, and are very unstable even in the dry state.

Bromate of Strontium. $2SrBrO^3 + aq.$—Small shining rhomboïdal prisms, with truncated lateral edges, isomorphous with the barium-salt. Ratio of axes = 1 : 1·1642 : 1·2292. Inclination of clino-diagonal to principal axis = 89°. The crystals dissolve in 3 pts. of water at ordinary temperatures; do not lose weight over sulphuric acid, become anhydrous at 120° C., and at a higher temperature are quickly resolved into oxygen gas and bromide of strontium.

Bromates of Tin.—*Stannic hydrate* unites slowly with bromic acid, and forms, after drying over oil of vitriol, a vitreous mass, which loses 18 per cent. in weight at 180° C. *Stannous chloride* forms a white precipitate with bromate of potassium.

Uranic Bromate.—A solution of uranic hydrate in bromic acid yields, by evaporation over oil of vitriol, a yellow uncrystallisable syrup which decomposes by evaporation, giving off bromine and leaving a basic salt.

Bromate of Yttrium.—Sparingly soluble in water; remains in the anhydrous state when its solution is evaporated.

Bromate of Zinc. $ZnBrO^3 + 3\,aq.$ — Regular octahedrons modified by cube-faces; isomorphous with the magnesium-salt. It dissolves in 1 pt. water at ordinary temperatures, is permanent in the air, melts in its water of crystallisation at 100° C., and becomes anhydrous at 200°, but undergoes decomposition at the same time, giving off bromine-vapour and oxygen, and leaving pulverulent oxide of zinc. The salt is decomposed by a small quantity of ammonia, but dissolves completely in excess of ammonia, the solution yielding by evaporation over hydrate of potassium:

Ammonio-bromate of zinc, or *bromate of zinc-ammonium*, $2NH^3ZnBrO^3 + 3\,aq.$ in small prismatic crystals, which, when exposed to the air, become moist and yellow, and smell of free bromine. Water and alcohol decompose them with separation of hydrate of zinc. At a gentle heat, the salt decomposes with a loud hissing noise, and gives off bromine together with nitrogen gas and water.

BROMIC SILVER. Native bromide of silver. (See Silver.)

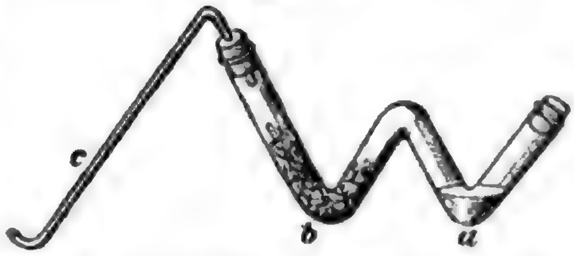
BROMIDES. Compounds of bromine with electro-positive radicles. Bromine, like chlorine, is monatomic, 1 at. of it being capable of uniting with 1 at. of hydrogen or other monatomic radicle, 2 at. of bromine with 1 at. of a diatomic radicle, *e.g.* bromide of ethylene $(C^2H^4)''Br^2$, 3 at. of bromine with 1 at. of a triatomic radicle, *e.g.* bromide of glyceryl $(C^3H^5)'''Br^3$. Bromine is less powerfully electro-negative than chlorine; consequently bromides are for the most part decomposed by chlorine.

Bromide of Hydrogen. Hydrobromic or Bromhydric Acid. HBr.—This compound is gaseous at ordinary temperatures, and is composed of equal measures of bromine-vapour and hydrogen united without condensation. It is not readily formed by the direct union of its elements. A mixture of hydrogen and bromine-vapour does not unite when exposed to the sun's rays; neither does it explode when a red-hot wire or a burning taper is introduced into it; but combination takes place slowly in the immediate neighbourhood of the hot body, and more quickly when the mixture of bromine and hydrogen is passed through a red-hot tube, or when a platinum wire immersed in it is kept red-hot by the electric current.

Preparation.—1. By the action of water on tribromide of phosphorus:

$$PBr^3 + 3H^2O = H^3PO^3 + 3HBr.$$

Fig. 113.



A few grammes of bromine are introduced into the bend *a* of the apparatus (*fig.* 113), and in the bend *b* are placed some small pieces of phosphorus, moistened with water, and separated by pounded glass. The bromine at *a* is gently heated by a spirit-lamp, and the vapour passing over to *b* forms bromide of phosphorus, which is immediately decomposed by the water, yielding phosphorous acid, which remains in the tube, and hydrobromic acid, which passes on through the delivery-tube *c*, and may be collected over mercury.—2. By decomposing bromide of sodium or potassium with strong sulphuric acid:

$$2NaBr + H^2SO^4 = Na^2SO^4 + 2HBr.$$

The hydrobromic acid thus produced is, however, mixed with vapour of bromine and sulphurous anhydride, produced in the manner represented by the equation:

$$2NaBr + 2H^2SO^4 = 2Br + SO^2 + 2H^2O + Na^2SO^4;$$

the bromine may be separated by agitation with mercury; but the sulphurous anhydride is not easily removed.—3. The aqueous solution of the acid may be prepared by decomposing a solution of bromide of barium with sulphuric acid diluted with an equal weight of water, and distilling the filtered liquid.—4. Also by passing sulphuretted hydrogen into a mixture of bromine and water:

$$10Br + 2H^2S + 4H^2O = 10HBr + H^2SO^4 + S$$

The liquid is filtered to separate the precipitated sulphur, and the hydrobromic acid separated from the sulphuric acid by distillation.—5. By the action of bromine on hydriodic acid, on aqueous ammonia, and on many organic compounds, naphthalin, for example.

Properties.—Colourless gas having a very pungent odour, which excites coughing, and a strongly acid taste. Reddens litmus strongly, and excites itching and inflammation when applied to the skin. Fumes in the air more strongly than hydrochloric acid. Specific gravity, by experiment, 2·71 (Löwig); by calculation $\frac{80 + 1}{2} = 40{\cdot}5$, compared with hydrogen, or $40{\cdot}5 \times 0{\cdot}0693 = 2{\cdot}801$ compared with air. Liquefies at −92° F. (−69° C.), and solidifies at −100° F. (−73° C.) (Faraday). It is rapidly and copiously absorbed by water, forming a strongly acid solution, which, when saturated, has a density of 1·29, and fumes strongly in the air. This saturated solution boils at a temperature below 100° C., giving off the gas, and is thereby rendered weaker: a more dilute acid boils at a temperature above 100°, and a very dilute acid becomes stronger by boiling.

Decompositions.—1. The gas is not decomposed by heat alone.—2. *Potassium* introduced into it, even at ordinary temperatures, decomposes it completely, forming bromide of potassium, and leaving a volume of pure hydrogen equal to half that of the original gas. Tin produces the same effect when aided by a gentle heat. This reaction determines the composition of the acid; for the weight of 1 vol. of the gas (the observed specific gravity) diminished by the weight of half a volume of hydrogen, gives a number which is very nearly half the observed specific gravity of bromine (5·54 according to Mitscherlich):

$$2{\cdot}71 - \frac{0{\cdot}0693}{2} = 2{\cdot}68 = \frac{5{\cdot}36}{2}$$

Hence the gas is composed of equal volumes of bromine and hydrogen, united without condensation.—3. The gas, or its aqueous solution, is immediately decomposed by *chlorine*, hydrochloric acid being formed and bromine separated, recognisable by its red colour. *Iodine*, on the contrary, does not decompose hydrobromic acid. Hence the affinity of bromine for hydrogen is, under similar circumstances, less than that of chlorine, and greater than that of iodine.—4. The acid is also decomposed by *oxygen* and by highly oxidised bodies. The aqueous solution turns brown on exposure to the air, from separation of bromine, which remains dissolved. *Nitric acid* also separates the bromine, especially on heating the liquid. The mixture of the two acids dissolves gold, like nitrohydrochloric acid. Strong *sulphuric acid* decomposes it, yielding sulphurous anhydride, bromine, and water:

$$H^2SO^4 + 2HBr = SO^2 + 2H^2O + Br^2.$$

With *bromic acid*, it yields water and free bromine:

$$HBrO^3 + 5HBr = 3H^2O + Br^6.$$

5. With metallic *protoxides*, it forms water and a bromide of the metal: *e.g.* $2HBr + Ag^2O = 2AgBr + H^2O$. With *peroxides*, a similar decomposition takes place, attended also with evolution of bromine: *e.g.* $2HBr + MnO = MnBr + H^2O + Br$.

Combinations. — Hydrobromic acid unites directly with *ammonia* NH^3, forming hydrobromate of ammonia, $NH^3.HBr$, or bromide of ammonium, NH^4Br. Similarly with the compound ammonias, *methylamine*, *ethylamine*, &c., and with *phosphoretted hydrogen*. The aqueous solution dissolves certain *metallic oxides*, viz. the alkalis and earths, forming solutions, which may be supposed to contain hydrobromates of those oxides. It unites with many *hydrocarbons*, *e.g.* with oil of turpentine, forming the compound $C^{10}H^{16}.HBr$.

Bromides, Metallic. MBr. — Bromine unites directly with most metals. Potassium, arsenic, antimony, and tin unite with liquid bromine, producing vivid combustion; bismuth, iron, and mercury combine with it at ordinary temperatures without combustion; but on the application of heat, combustion takes place. Gold combines gradually with bromine at ordinary temperatures; platinum does not. With many metals, the application of heat is necessary to induce combustion. Bromides are also formed by the action of metals on hydrobromic acid gas (p. 672). Vapour of bromine passed over ignited potash, soda, baryta, or lime, forms a bromide of the metal and eliminates the oxygen; bromine decomposes oxide of silver, even at ordinary temperatures. Carbonates are also readily decomposed by it.

Nearly all bromides are soluble in water; bromide of lead however dissolves very sparingly, and bromide of silver and mercurous bromide are quite insoluble. The soluble bromides may all be produced by the action of hydrobromic acid on the corresponding oxides or carbonates; and on evaporating the solutions, water is in most cases given off, the metallic bromide remaining. Some of them, however, viz. the bromides of magnesium, aluminium, and the other earth-metals, are more or less decomposed during the evaporation of the solutions, giving off hydrobromic acid and leaving a mixture of bromide and oxide of the metal.

Metallic bromides are solid at ordinary temperatures; most of them fuse at a moderate heat, and volatilise at higher temperatures. They strongly resemble the chlorides. The bromides of gold and platinum are decomposed by mere exposure to heat; many others give up their bromine when heated in contact with the air. Chlorine, with the aid of heat, drives out the bromine and converts them into chlorides. Hydrochloric acid also decomposes them at a red heat, giving off hydrobromic acid. Strong sulphuric or nitric acid decomposes them, with evolution of hydrobromic acid, which, if the sulphuric or nitric acid is concentrated and in excess, is partly decomposed, with separation of bromine and formation of sulphurous anhydride or nitric oxide (p. 672). Bromides heated with sulphuric acid and peroxide of manganese or chromate of potassium, give off free bromine. If the bromide is quite pure, the evolved bromine is completely decolorised by ammonia; but if chlorine is also present, cholorochromic acid distils over, together with the bromine, and the distillate then forms a yellow liquid with ammonia.

Bromides in solution are easily decomposed by chlorine, either in the form of gas or dissolved in water, the liquid acquiring a red or reddish-yellow colour, according to the quantity of bromine present; and on agitating the liquid with ether, that liquid dissolves the bromine, forming a red solution, which rises to the surface. (See BROMINE.

Soluble bromides give with *nitrate of silver*, a white precipitate of bromide of silver, greatly resembling the chloride, but much less soluble in ammonia; insoluble in hot nitric acid. *Mercurous nitrate* produces a yellowish-white precipitate; and *acetate of lead*, a white precipitate much less soluble in water than the chloride. *Nitrate of palladium* produces in solutions of bromides not containing chlorine, a black precipitate of bromide. Chloride of palladium produces no precipitate; neither does the nitrate, if soluble chlorides are present.

Bromides of Organic Radicles. Bromine unites with organic radicles both basic and acid. The compounds are formed in the same manner as the corresponding chlorides, which they also resemble in most of their properties, though they are less volatile. They contain, in two volumes of vapour, one, two, or three volumes of bromine-vapour, according as the organic radicle which they contain is mono-, di-, or tri-atomic, *e. g.*:

2 vol.	bromide of	trityl	C^3H^7Br	contain	1 vol. bromine
„	„	tritylene	$(C^3H^6)''Br^2$	„	2 vol. „
„	„	glyceryl	$(C^3H^5)'''Br^3$	„	3 vol. „

1. The *bromides of the alcohol-radicles, hydrobromic or bromhydric ethers,* are obtained by distilling the corresponding alcohols with hydrobromic acid or bromide of phosphorus: *e. g.*:

$$\underset{\text{Alcohol.}}{C^2H^5.H.O} + PBr^3 = \underset{\text{Bromide of ethyl.}}{C^2H^5Br} + HBr + \underset{\text{Oxybromide of phosphorus.}}{PBr^3O}$$

Distilled with alkalis, they yield the corresponding alcohol and a bromide of the alkali-metal.

2. The *bromides of acid-radicles* are produced by the action of bromide of phosphorus on the corresponding acids, or by the action of chlorides of acid-radicles on certain metallic bromides: *e. g. bromide of acetyl*, $C^2H^3O.Br$; *bromide of succinyl*, $(C^4H^4O^2)''Br^2$. Alkalis decompose them, with formation of a metallic bromide, and a salt of the corresponding organic acid, *e. g.*:

$$\underset{\text{Bromide of succinyl.}}{(C^4H^4O^2)''Br^2} + 2KHO = \underset{\text{Succinate of potassium.}}{C^4H^4O^2.K^2.O^2} + KBr.$$

3. The *bromides of aldehyde-radicles* are monatomic bromides of the general form, $C^nH^{2n-1}Br$: *e. g. bromide of vinyl*, C^2H^3Br. They are isomeric with the monobrominated diatomic alcohol-radicles, *e.g.* C^3H^5Br, with bromotritylene, $C^3{}^{H^5}_{Br}$. They are volatile liquids, obtained by the action of alcoholic potash on the bromides of the diatomic alcohol-radicles: their properties and reactions are analogous to those of the corresponding chlorides (*q. v.*)

4. Many other organic radicles, such as oil of turpentine, its isomers and homologues, likewise unite with bromine and with hydrobromic acid, forming definite compounds, sometimes liquid, sometimes crystalline, *e.g. bromide of cajputene*, $C^{10}H^{16}Br^4$; *hydrobromate of turpentine-oil*, $C^{10}H^{16}.HBr$, &c.

BROMINDAMITE. See the next article.

BROMINDOPTENE. The name of a doubtful compound, which Erdmann obtained, together with bromisatin and dibromisatin, by the action of bromine on indigo. It was resolved by potash into bromindoptic (bromophenissic) acid, and a volatile body, called by Erdmann bromindamite, but doubtless identical with tribromophenylamine. (Handw. d. Chem. 1te Aufl. iv. 22.)

BROMINE. *Symbol* Br. *Atomic weight* 80.—This element was discovered in 1826 by Balard, who extracted it from the mother-liquor of the salt-marshes of Montpellier. It exists in sea-water; in the water of many salt-springs, especially in that of Theodorshall, near Kreuznach in Prussia, whence a large portion of the bromine of commerce is obtained; and, together with iodine, in the ash of sea-weed (*soude de varech*), whence larger quantities are extracted; also in sponges and many marine animals. As bromide of silver, it is found native in Mexico and Chili, and at Huelgoeth in Bretagne; very small quantities are found in Silesian zinc-ore and in English rock-salt.

Preparation.—1. *From the mother-liquor of sea-water or saline-springs.* After these waters have been freed by crystallisation from the greater part of the chlorides and sulphates of sodium and potassium, the remaining liquid contains bromine, chiefly in the form of bromide of magnesium. This liquid is mixed in a retort with peroxide of manganese and hydrochloric acid, and distilled. Chlorine is then evolved in the liquid, and decomposes the bromide of magnesium, setting free the bromine, which distils over into the receiver, in the form of a heavy dark-red liquid, surmounted by an aqueous solution of bromine.—2. *From the mother-liquor of varec.* This liquid contains iodine and bromine, in the proportion of about 1 pt. bromine to 8 iodine. The iodine is first precipitated either by passing chlorine gas into the liquid, till a sample taken out gives no precipitate either with chlorine-water or with iodide of potassium; or it is precipitated as free iodine and cuprous iodide, by adding cupric sulphate to the liquid: ($Cu^2SO^4 + 2NaI = Na^2SO^4 + Cu^2I + I$). The remaining liquid is then mixed with peroxide of manganese and strong sulphuric acid (the requisite proportions being first determined by trial on a small quantity) and distilled. The bromine then passes over as before, the decomposition being effected in the manner shown by the equation:

$$2MgBr + 2MnO + 2H^2SO^4 = Br^2 + Mg^2SO^4 + Mn^2SO^4 + 2H^2O.$$

The bromine which collects at the bottom of the receiver in either mode of preparation, is separated from the supersaturated aqueous solution by means of a tap-funnel, and further purified by distillation in contact with chloride of calcium. The aqueous solution is shaken up with ether; the red ethereal solution of bromine which rises to the top is treated with caustic potash, till its colour disappears, whereby bromide and bromate of potassium are produced; the liquid is evaporated to dryness; and the residue is ignited in a crucible, to convert the bromate $KBrO^3$, into bromide KBr. The whole quantity thus obtained is decomposed by distillation with peroxide of manganese and sulphuric acid, whereby the remaining quantity of bromine is obtained in the free state.

Commercial bromine is generally contaminated with chlorine, derived either from that which is used to separate it, or from the mother-liquor itself. It may be purified by saturating it with hydrate of barium, whereby bromide, chloride, bromate, and hypochlorite of barium are formed; evaporating and igniting to decompose the oxygen-salts; and treating the residue with alcohol, which dissolves the bromide of barium and leaves the chloride. The pure bromide is then decomposed with sulphuric acid and peroxide of manganese, as above.

Properties.—Bromine is, at ordinary temperatures, a liquid of a deep brown-red colour. It has a peculiar irritating, disagreeable odour; whence its name (*βρῶμος*), and a repulsive taste. It is highly poisonous; a drop placed on the beak of a bird is sufficient to destroy life. Specific gravity 2·966 (Balard); between 2·98 and 2·99 at 15° C. (Löwig); 3·1872 at 0° C. (Pierre). It is a non-conductor of electricity. At −22° C. it solidifies, forming a hard, brittle, laminated mass, having a dark lead-grey colour, and semi-metallic lustre: it retains the solid state for a long time, even at −12° C. It is very volatile; a few drops thrown into a large flask speedily fill it with red vapours. It boils at 63° C. (Pierre); at 58° (Andrews); at 45° (Löwig). Vapour-density 5·54 (Mitscherlich); by calculation, 80 compared with hydrogen; 5·544 (= 80 × 0·0693), compared with air.

Bromine dissolves sparingly in water, more readily in alcohol, and in all proportions in ether. With water at 0° C. it forms a solid hydrate, $Br . 5H^2O$, which is not decomposed between 15° and 20°.

Bromine resembles chlorine in many of its properties. It has a powerful affinity for hydrogen, though not quite so strong as that of chlorine, and hence it acts with energy upon many organic substances. It is a powerful bleaching agent, and corrodes wood and cork, first turning them yellow. A small quantity of it imparts a transient yellow colour to the skin; a larger quantity stains it permanently yellow, then brown, and a still larger quantity produces immediate corrosion and violent inflammation. It colours starch orange-yellow. It decomposes vapour of water when passed with it through a tube heated to bright redness, yielding hydrobromic acid and oxygen. A burning taper introduced into vapour of bromine, burns for an instant with a green light, and is then extinguished.

Bromine decomposes phosphoretted hydrogen, sulphydric acid, hydriodic acid, and metallic iodides, but the resulting bromine-compounds are decomposed by chlorine.

Bromine acts readily on many organic compounds, removing part of the hydrogen in the form of hydrobromic acid, while another portion of bromine takes the place of the hydrogen thus abstracted, 80 pts. bromine being always introduced for every 1 pt. of hydrogen removed. In this manner, bromacetic acid, $C^2H^3BrO^2$, and a considerable number of other brominated compounds, are formed.

Bromine unites with all the elementary bodies, and with many compound radicles. In all its compounds, except those with chlorine, fluorine, oxygen, and perhaps sulphur, it plays the part of the chlorous or electro-negative element. In this respect, it is intermediate between chlorine and iodine, expelling the latter from its combinations with positive radicles, and being itself expelled by the former (see BROMIDES, p. 672). We shall here describe only those compounds in which the bromine is electro-positive, viz. the chlorine, fluorine, oxygen, and sulphur-compounds: the others are described under the several positive radicles.

BROMINE, CHLORIDE OF. Bromine absorbs a large quantity of chlorine gas, forming a reddish-yellow, mobile liquid, very volatile, and giving off dark-yellow, strong-smelling, and tear-exciting vapours, which exert a powerful bleaching action, and in which metals burn quickly to chloride and bromide.

When chloride of bromine is mixed with a small quantity of water, and cooled to 0° C., or when gaseous chloride of bromine is passed through a glass tube moistened with water, the hydrated chloride of bromine is formed, which crystallises in needles or laminæ, and melts at 7° C. to a light yellow liquid. It is decomposed by ammonia, forming nitrogen gas, chloride of nitrogen, and bromide of ammonium. Chloride of bromine dissolves with yellow colour in water. The same solution is obtained by dissolving bromine in saturated chlorine-water; it has the odour and bleaching action of chloride of bromine; decomposes in sunshine into hydrochloric and bromic acids, and is decomposed in like manner by aqueous alkalis, yielding a chloride and a bromate of the alkali-metal. The aqueous solution is decomposed by ether, which separates and dissolves the bromine. (Handw. d. Chem. ii. [2] 475.)

BROMINE, DETECTION AND ESTIMATION OF. 1. *Reactions.*—Free bromine is recognised by its odour, the deep-red colour of its vapour, and the orange-yellow colour which it imparts to gelatinous starch. When it exists in aqueous solution in too small quantity to be recognised immediately, it may be separated by shaking up the liquid with ether, and proceeding as described below.

Bromine in the state of hydrobromic acid or a soluble metallic bromide, is detected by the reactions already described (pp. 672, 673). Small quantities of bromine are most easily recognised by cautiously adding chlorine-water till the solution assumes a red or yellow tint; if too much chlorine be added, chloride of bromine will be formed, which is colourless. On shaking the solution with ether, that liquid dissolves the bromine, and rises to the surface in the form of a red stratum. This may be separated by a pipette, or tap-funnel; neutralised with potash, which decolorises it, converting the bromine into bromide and bromate of potassium; and evaporated to dryness in a porcelain crucible. On igniting the residue, to convert it all into bromide, then introducing it into a test-tube, and heating with sulphuric acid and peroxide of manganese, bromine is given off in red vapours, which, if led into a solution of starch, colour it orange-yellow.

The presence of chlorides does not interfere with this reaction; if, however, the quantity of chlorine is very large compared with that of the bromine, as in saline waters, it is best to concentrate the solution till the greater part of the chlorides crystallise out, and search for bromine in the mother-liquor. If iodine is present, it must first be removed, either by precipitation with chloride of palladium, or by first adding just sufficient chlorine-water to precipitate the iodine, which is sure to be set free before the bromine: in fact, bromine itself separates iodine from its compounds; but the removal of the iodine is absolutely necessary, as its deep violet vapour would disguise the colour of the bromine, unless the quantity of the latter greatly predominated.

The methods of decomposing insoluble bromides will be given further on; likewise the methods of separating bromine from phosphorus, and other non-metallic elements. Bromates are reduced to bromides, either by ignition or by treatment with sulphurous or sulphydric acid.

2. *Quantitative Estimation.*—When bromine is present in a solution in the form of a bromide, it may be precipitated by nitrate of silver, the precipitate of bromide of silver being ignited in a porcelain crucible, with the same precautions as the chloride (see CHLORINE). It contains 42·55 per cent. bromine. If the solution is alkaline, it must be acidulated with nitric acid, added after the precipitation by nitrate of silver; if it were added before, a portion of the bromine might be set free and lost.

Insoluble bromides, *e.g. bromide of lead*, and *cuprous bromide*, may be decomposed by suspending them in water, and passing sulphuretted hydrogen through the liquid. The metal is then converted into sulphide, while hydrobromic acid remains dissolved together with excess of sulphydric acid. This excess may be removed by addition of ferric sulphate, which precipitates sulphur, and in the filtered liquid the bromine may be estimated, as above, by precipitation with nitrate of silver. *Bromide of silver* may also be decomposed by fusion with carbonate of sodium, or, better, with a mixture of carbonate of sodium and carbonate of potassium in equivalent proportion, in a porcelain crucible. The silver is thereby reduced to the metallic state, and may be weighed after washing. The bromine is then estimated by loss.

Another method of decomposing bromide of silver, is to treat it with dilute sulphuric acid and pure metallic zinc. The silver is then reduced by the nascent hydrogen, and the bromine passes into the solution as bromide of zinc. The silver may then be washed and weighed as before. This method, however, is not quite exact (see CHLORINE).—*Mercurous bromide* may be completely decomposed by a solution of pure caustic potash, a solution of bromide of potassium being formed, from which the bromine may be precipitated by nitrate of silver with addition of nitric acid.

Many *oxybromides* which are insoluble in water, are soluble in nitric acid. The acid should be dilute, and if heat is required, the materials must be placed in a flask having a glass stopper, and the heat kept as low as possible, otherwise bromine will escape. The bromine may then be thrown down as bromide of silver.

Volatile bromides, such as the bromides of sulphur, phosphorus, arsenic, and antimony, are completely decomposed by water, the bromine being converted into hydrobromic acid, from which it may be precipitated by nitrate of silver.

Bromates must be reduced to bromides by sulphurous or sulphydric acid; the bromine may then be precipitated by silver-solution, after the excess of the reducing agent has been removed by a ferric salt. Bromates may also be converted into bromides by ignition.

The quantity of *free bromine* in a solution, is estimated by treating it with excess of ammonia, whereby it is completely converted into bromide of ammonium, with evolution of nitrogen. The diluted solution is then treated with nitrate of silver.

Estimation of Bromine in presence of Chlorine.—There is no known method of effecting a complete separation of these elements, and when they occur together, their amounts must be estimated by an indirect method. This is effected by precipitating them both together by nitrate of silver; fusing and weighing the entire precipitate in a porcelain crucible; then remelting it; taking out a convenient portion on the end of a glass rod; cutting it when cold into small shavings; introducing them into a bulb-tube; and igniting them, after weighing, in a current of dry chlorine. The whole of the bromine is then expelled, provided the stream of chlorine is kept up for some time, and nothing but chloride of silver remains. This is weighed, and from its weight, and that of the mixture of chloride and bromide before decomposition, the quantities of chlorine and bromine may be found. For the difference of the weights (d) is clearly the difference between the weight of the bromine expelled and that of the chlorine which has taken its place; and for every 80 pts. of bromine expelled 35·5 pts. of chlorine have come in: hence we have the equations:

$$\mathrm{Br} - \mathrm{Cl} = d : \qquad \frac{\mathrm{Br}}{\mathrm{Cl}} = \frac{80}{35{\cdot}5}$$

$$\text{whence:} \qquad \mathrm{Br} = \frac{80}{80 - 35{\cdot}5}\, d = 1{\cdot}796\, d$$

that is to say: to find the quantity of bromine, *multiply the difference of the weights by* 1·796.

If the quantity of bromine is very small compared with the chlorine, this method does not give exact results. In that case, it is necessary to *concentrate the bromine*, that is, to increase the proportion of it in the precipitate subjected to the experiment. Now when a mixture containing a large quantity of soluble chloride with a small proportion of bromide, is treated with about one-sixth of the quantity of nitrate of silver required for complete precipitation, the whole of the bromine is precipitated, together with a portion of the chlorine. The liquid must be briskly agitated to cause the precipitate to settle down, but no heat must be applied. The precipitate is then to be ignited, weighed, and decomposed in a stream of chlorine in the manner just described. The remainder of the chlorine, now free from bromine, is precipitated as chloride of silver in the usual way. Another method of concentrating the bromine in a mixture of chloride of sodium containing a small quantity of bromide, is to treat the dry mixture with very strong alcohol, which dissolves the whole of the bromide of sodium, but only a small portion of the chloride. The filtered alcoholic solution is then evaporated, the residue is dissolved in water, and the bromine and chlorine are precipitated by nitrate of silver and estimated as before. To estimate the quantity of bromine in sea-water or a brine-spring, the liquid must be evaporated to dryness, a weighed quantity of carbonate of sodium having been previously added to prevent the loss of bromine and chlorine which might arise from the decomposition of the chloride and bromide of magnesium during the evaporation, and the dry residue treated with alcohol as above.

Estimation of Bromine in presence of Iodine.—The iodine is precipitated by chloride of palladium (or by the nitrate, if chlorides are present, p. 674), the excess of palladium removed by sulphuretted hydrogen, the excess of this last reagent by nitric acid or a ferric salt, and the bromine then precipitated by nitrate of silver.

(For other modes of estimation, see CHLORINE and IODINE.)

Field (Chem. Soc. Qu. J. x. 234) has shown that chloride of silver is completely decomposed by digestion with solution of bromide of potassium, the chlorine and bromine changing places; and that both bromide and chloride of silver are decomposed in like manner by iodide of potassium. Hence, if a solution containing chlorine, iodine, and bromine, be divided into three equal parts; each portion precipitated by nitrate of silver; the first precipitate dried and weighed; the second digested with bromide of potassium, then dried and weighed; and the third with iodide of potassium, then dried and weighed, the relative quantities of the three elements may be determined by an extension of the method of calculation above given (see also p. 224). Let the weights of the three precipitates be w, w', and w''; also let the atomic weights of chloride, bromide, and iodide of silver be c, b, and i respectively, and the unknown quantities of chloride, bromide, and iodide of silver, x, y, and z; then we have the three equations:

$$x + y + z = w$$

$$\frac{b}{c}x + y + z = w'$$

$$\frac{i}{c}x + \frac{i}{b}y + z = w''$$

The first and second give: $$x = \frac{c(w - w')}{b - c}$$

Substituting this value in the second and third, they become:

$$y + z = w' - \frac{b(w - w')}{b - c} \quad [= p]$$

$$\frac{i}{b}y + z = w'' - \frac{i(w - w')}{b - c} \quad [= q]$$

whence: $$y = \frac{b(q - p)}{i - b}$$

and: $$z = w - (x + y).$$

For the volumetric estimation of bromine, see ANALYSIS, VOLUMETRIC (p. 267). For the estimation of bromine in organic compounds, see ANALYSIS, ORGANIC (p. 247).

3. *Atomic Weight of Bromine.*—The older determinations of the atomic weight of bromine were much too low. Balard estimated it at 75·8, Liebig at 75·2, Berzelius at 78·2. The most exact determinations are due to Marignac (Biblioth. univ. de Genève, xlvi. 357), who found: 1. That 100 pts. pure silver dissolved in nitric acid and precipitated by bromide of potassium, yielded, as a mean, 174·065 pts. bromide of silver; whence, the atomic weight of silver being 108, that of bromine is $x = 74{\cdot}065 \times \frac{108}{100} = 79{\cdot}91$.—2. That 100 pts. silver required for precipitation, 110·36 pts. bromide of potassium; whence if Ag = 108 and K = 39·1, we have $100 : 110{\cdot}36 = 108 : 39{\cdot}1 + x$; whence $x = 80{\cdot}09$.—3. That 100 pts. bromate of potassium give off by ignition, on the average, 29·723 pts. oxygen, whence Br = 79·97. The mean of all these results is very nearly Br = 80, which is the number now universally adopted. Dumas arrived at the same result by igniting bromide of silver in chlorine gas, and determining the difference of weight thereby produced.

BROMINE, FLUORIDE OF. Fluorine is readily absorbed by bromine. The resulting compound, according to Leeson (Phil. Mag. Dec. 1844, p. 520) is liquid, easily soluble in water, and does not sensibly attack glass. It has been used as a means of accelerating the taking of photographic pictures by the electric light. (Compt. rend. xxxiii. 501.)

BROMINE, OXYGEN-ACIDS OF. The series of oxygen-compounds of bromine is by no means so complete as that of chlorine. No anhydrous oxide of bromine is known, and of the acids, only one has been obtained in the separate state and thoroughly examined, viz. Bromic acid, $HBrO^3$, already described (p. 669). All attempts to prepare a perbromic acid, analogous to perchloric acid, $HClO^4$, have been unsuccessful; but the existence of hypobromous acid, HBrO, is rendered probable by many experiments, though neither the acid itself, nor any of its salts, have yet been obtained in definite form.

When mercuric oxide is added to bromine-water, a sparingly soluble oxybromide of mercury is formed, together with a bleaching liquid, which, by distillation in vacuo, yields a liquid supposed to be *hypobromous acid* (Balard). According to Gay-Lussac, *hypobromous anhydride* may be obtained in the gaseous state in the same manner as hypochlorous anhydride. (See CHLORINE, OXIDES OF.)

When bromine is added to cold dilute aqueous alkalis, a metallic bromide is formed, together with a very small quantity of bromate, and a liquid, which does not smell of bromine, bleaches litmus and indigo and vegetable colours in general, and gives off nitrogen in contact with ammonia. On heating the liquid, no bromine is evolved, but a bromate is formed and the bleaching power is destroyed. These phenomena are precisely analogous to those which are exhibited when chlorine is dissolved in cold alkaline solutions. (See HYPOBROMOUS ACID.)

BROMINE, SELENIDE OF. See Selenium, Bromide of.

BROMINE, SULPHIDE OF. When bromine is brought in contact with flowers of sulphur at ordinary temperatures, a dark brown, fuming, oily liquid is formed, having an odour like that of sulphide of chlorine. It is not altered by cold water; but water at 10° C. decomposes it with slight explosion, forming sulphuric, hydrobromic, and sulphydric acids. When it is distilled, the first third of the distillate appears to consist of Br^2S^2, while the liquid remaining in the retort is a mixture of this compound with another sulphide of bromine, and, even when the distillation is completed, there still remains a viscid liquid containing bromine. (H. Rose, Pogg. Ann. xxviii. 550.)

BROMIODOFORM. $CHBr^2I$.—This compound is produced by treating iodoform with bromine. It is a colourless liquid, which solidifies to a camphorated mass at 0° C.; melts at $+6°$; is very volatile; has a penetrating odour and saccharine taste. It may be regarded as *dibrominated iodide of methyl.* (Sérullas, Ann. Ch. Phys. [2] xxxiv. 225; xxxix. 97.—Bouchardat, J. Pharm. xxiii. 10.)

BROMISATIC ACID. See Isatic Acid.

BROMISATIN. See Isatin.

BROMITE. Native bromide of silver, found in Mexico and in Chili. (See Silver, Bromide of.)

BROMITONIC ACID. See Citraconic Acid, Decompositions of.

BROMLITE. Syn. with Alstonite.

BROMO-COMPOUNDS or **BROMINATED COMPOUNDS.** Compounds resulting from the substitution of bromine for hydrogen, chiefly in organic bodies. They are produced by the action of bromine or of bromide of phosphorus on alcohols, acids, hydrocarbons, &c. Most of them are described under the several principal compounds, *e.g.* Bromobrucine under Brucine, &c.

BROMOFORM. $CHBr^3$.—Produced by the simultaneous action of bromine and caustic potash on wood-spirit, alcohol, or acetone; also by the action of bromine on aqueous citric or malic acid; and by decomposing bromal with alkalis. It is a limpid liquid of specific gravity 2·13, having an agreeable odour and saccharine taste. It is less volatile than chloroform, very little soluble in water, to which, however, it imparts its taste and odour; soluble in alcohol, ether, and essential oils. It dissolves small quantities of sulphur and phosphorus, and a large quantity of iodine. It burns with difficulty. When its vapour is passed through a red-hot tube, it is resolved into charcoal and bromine-vapour. Boiling potash-ley decomposes it more easily than chloroform, yielding formate and bromide of potassium. (Löwig, Ann. Ch. Pharm. iii. 295.—Dumas, Ann. Ch. Phys. [2] lvi. 120.)

BROMOPICRIN. CBr^3NO^2.—A product obtained by distilling picric acid with hypobromite of calcium (p. 923).

BROMOSAMIDE. See Salicylamide.

BROMOTRICONIC ACID. } See Citric and Citraconic Acids, Decompositions by bromine.
BROMOXAFORM. }

BROMUS. A genus of grasses. The ashes of *Bromus erectus* and *Bromus mollis* have been analysed by Way and Ogston (Journal of the Royal Agr. Soc. [2] xii. 530). 100 pts. of *Br. erectus* (air-dried) yielded 59·6 per cent. water, and 2·1 ash; of *Br. mollis*, 76·6 per cent. water and 1·4 ash.

100 pts. of ash were found to contain:

	K^2O	Na^2O	Ca^2O	Mg^2O	Fe^4O^3	SO^3	SiO^2	CO^2	P^2O^5	KCl	NaCl
Br. erectus . .	20·3	. .	10·4	5·0	0·26	5·5	38·5	0·5	7·5	10·6	1·4
Br. mollis . .	30·1	0·3	6·6	2·6	0·21	4·9	33·3	9·1	9·6	. .	3·1

BROMYRITE. Native bromide of silver. See Silver.

BRONZE. An alloy of copper and tin. See Copper.

BRONZITE. *Schillerspar. Diallage fibro-laminaire.*—A mineral belonging to the augite family (p. 476). It is massive, with laminar structure inclining to fibrous. Colour varying from yellowish-brown to pinchbeck-brown. Lustre from mother-of-pearl to bright adamantine (pseudo-metallic). Harder than felspar. Specific gravity 3·201 to 3·25. Like all the augites, it is a metasilicate, its general formula being M^2SiO^3 or $M^2O.SiO^2$, the M^2O denoting lime, magnesia, manganous oxide, and ferrous oxide in variable proportions, the magnesia, however, predominating. It is found in large masses in beds of serpentine.

Delesse examined a mineral from the serpentine of Houx in the Vosges, which resembled bronzite in its large amount of magnesia (56·33 Si^2O; 1·50 Mn^4O^3 and Cr^4O^3; 6·73 Fe^2O; 31·93 Mg^2O; 1·40 Ca^2O; 2·11 loss by ignition); but differed from it in not possessing the same metallic lustre and pinchbeck-brown colour, and in being less distinctly cleavable, especially parallel to oP; specific gravity 3·154 (Ann. Min. [4] xviii. 318). (For other analyses of bronzite, see Gm. Handb. iii. 403, 404; Garrett, Sill. Am. J. [2] xv. 333; Kjerulf, Bischof's Lehrb. d. chem. u. phys. Geolog. ii. 1495.)

BROOKITE. *Jurinite. Arkansite.*—One of the forms of native titanic anhydride TiO^2, which is trimorphous. The crystals belong to the trimetric system, and generally exhibit very complicated combinations, among which we may assume, as the primary form, the pyramid P, in which the lengths of the brachydiagonal, macrodiagonal, and principal axis, are to one another, as 0·5951 : 1 : 0·5558. Angle of the terminal edges in the brachydiagonal section = 135° 46′; in the macrodiagonal section = 101° 37′; and of the lateral edges = 94° 44. The crystals exhibit, together with P, the faces $\infty\bar{P}\infty$ and $\infty\breve{P}2$, likewise other pyramids and horizontal prisms; and are often reduced to the tabular form by predominance of the faces $\infty\breve{P}\infty$. Cleavage parallel to $\infty\bar{P}\infty$. Yellow, red, brown, or black, with adamantine or semi-metallic lustre. Transparent to opaque. Streak yellowish-white. Hardness = 5·5 to 6·0. Specific gravity = 3·85 to 4·22. Brittle. It is found at Oisans in Dauphiné, at Tremadoc in Wales, on the St. Gothard, in the Valorsina and the Griesernthal in Switzerland, at Miask in the Ural, and at Magnet Cove in Arkansas. The crystals from the last-mentioned locality, were at first regarded as a distinct species, called *Arkansite.* (Kopp, Handw. d. Chem. ii. [2] 521; Krystallographie, p. 256.)

BROSSITE. A variety of bitterspar from the Brossa valley in Piedmont and other localities, distinguished by a rather large amount of iron. A specimen from Traversella, analysed by Hirzel (Zeitsch. f. Pharm. 1850, p. 24), yielded 11·13 per cent. ferrous carbonate.

BROUSONETTIA TINCTORIA or *Morus tinctoria.* — The plant which yields yellow-wood. (See MORUS and MORINTANNIC ACID.)

BROWN BERRIES. — The fruit of *Rubus fructicosus.* See RUBUS.

BRUCINE. *Canimarine. Vomicine.*—$C^{23}H^{26}N^2O^4 + 4H^2O$ (Pelletier and Caventou (1819), Ann. Ch. Phys. [2] xii. 118; xxvi. 53.—Pelletier and Dumas, *ibid.* xxiv. 176.—Corriol, J. Pharm. xi. 495.—Liebig, Ann. Ch. Phys. [2] xlvii. 172; Ann. Ch. Pharm. xxxi. 50.—Regnault, Ann. Ch. Phys. [2] lxviii. 113). This vegetable alkaloid exists, together with strychnine, in nux vomica (the seed of *Strychnos nux vomica*), in the bean of St. Ignatius (the seed of *Strychnos Ignatii*), in the wood of *Strychnos Colubrina*, and in *upas tieute*, an extract prepared from the bark of the *Strychnos tieute*, and used by some of the natives of the East Indian Archipelago, for poisoning their arrows. It also exists in large quantity, and unaccompanied by strychnine, in false angustura bark, originally supposed to be the bark of *Brucia antidysenterica*, but now ascertained to belong to a species of strychnos, probably *Strychnos nux vomica.*

Preparation.—1. *From false angustura bark.*—The pulverised bark is treated with ether to remove fatty matter, then digested in strong alcohol; the dry alcoholic extract is dissolved in water; the colouring matter precipitated by subacetate of lead; the excess of lead removed by sulphuretted hydrogen; and the liquid, which contains the brucine in solution, is boiled with magnesia, again filtered and evaporated. The brucine is thus obtained in the form of a granular mass, generally coloured. To purify this product, it is saturated with oxalic acid; the oxalate of brucine is washed with absolute alcohol cooled to 0° C. which dissolves the colouring matter, then redissolved in water, and decomposed by lime or magnesia; and the brucine thus set free, is redissolved in alcohol and crystallised by slow evaporation (Pelletier and Caventou). Thénard (Traité de Chimie, 6th ed. iv. 281), recommends as an economical mode of preparing brucine, to treat the bark with boiling water, add oxalic acid to the aqueous decoction, concentrate by evaporation, and purify the oxalate of brucine with cold alcohol, as above.

2. *From the seeds of Strychnos nux vomica, &c.* — The mother-liquors obtained in the preparation of strychnine from these seeds (see STRYCHNINE), contain brucine, which may be obtained from them by concentrating to the consistence of syrup, and slightly supersaturating with dilute sulphuric acid. The mixture, if left to itself for a few days, deposits crystals of sulphate of brucine, which are to be pressed, redissolved in boiling water, and decolorised by animal charcoal. The brucine is then separated by ammonia.

Properties.—Brucine crystallises by slow evaporation from its solution in hydrated alcohol, in oblique rhomboïdal prisms, often rather large, and sometimes agglomerated in heads like mushrooms. By rapid crystallisation from boiling water, nacreous laminated masses are obtained, having the aspect of boric acid. The crystals contain 4 at. water of crystallisation (= 15·45 per cent.); they effloresce quickly in dry air, and melt in their water of crystallisation at a little above 100° C. They dissolve in 850 pts. of cold, and 500 pts. of boiling water; they are very soluble in alcohol, sparingly in essential oils, insoluble in ether and in fat oils. The alcoholic solution turns the plane of polarisation to the left; specific rotatory power = $-61° 27'$. Acids diminish the rotatory power.

Brucine is poisonous, and acts on the animal economy like strychnine, but with much less energy.

Decompositions.—1. Strong *nitric acid* colours brucine deep red, forming a peculiar nitro-compound (cacotheline), and evolving nitrite of methyl, together with nitric oxide and carbonic anhydride, this last not being a direct product of the reaction, but resulting from the decomposition of oxalic acid previously formed. (Strecker, Ann. Ch. Pharm. xci. 76.)

$$C^{23}H^{26}N^2O^4 + 5HNO^3 = \underset{\text{Cacotheline.}}{C^{20}H^{22}N^4O^9} + \underset{\substack{\text{Nitrite of}\\ \text{methyl.}}}{CH^3.NO^2} + \underset{\substack{\text{Oxalic}\\ \text{acid.}}}{C^2H^2O^4} + 2NO + 2H^2O$$

The addition of protochloride of tin to the mixture changes the red colour to a fine violet. This, together with the red colour first produced, is quite characteristic of brucine, and serves to distinguish it from other alkaloids.—2. Strong *sulphuric acid* imparts to brucine, first a rose, then a yellow, and then a yellowish-green colour.—3. Brucine boiled with peroxide of lead and excess of sulphuric acid, forms a brown or red mass. This character further distinguishes brucine from strychnine, which, when treated with sulphuric acid and peroxide of lead, assumes a blue colour, changing through violet and red to yellow.—4. Brucine distilled with *sulphuric acid and peroxide of manganese*, gives off inflammable vapours and a liquid (probably hydrate of methyl), which burns with a blue flame; the same liquid is produced on treating brucine with mercuric oxide, or with sulphuric acid and chromate of potassium, carbonic and formic acids being likewise evolved in the latter case.—5. *Chlorine* does not produce immediate turbidity in a solution of brucine, but colours it yellow, and afterwards red; this last colour disappears after a while, the liquid at the same time depositing yellow uncrystallisable flakes.—6. *Bromine* dissolved in alcohol, quickly attacks brucine, colouring it violet. With a weak solution of bromine and sulphate of brucine, a resinous matter is formed, together with *bromobrucine*.—7. *Iodine* forms with brucine two peculiar compounds. Iodide of ethyl converts it into *hydriodate of ethylbrucine.*

Combinations.—The SALTS OF BRUCINE have a bitter taste, and are for the most part crystallisable. Strong nitric acid colours them red. They are decomposed, not only by mineral alkalis, but also by morphine and strychnine, which precipitate the brucine. When diluted with water and mixed with a slight excess of tartaric acid, they are not precipitated by acid carbonates of alkali-metals.

ACETATE OF BRUCINE is very soluble and uncrystallisable.

CHLORATE OF BRUCINE.—Transparent rhombs. Decomposes suddenly when strongly heated.

HYDROCHLORATE OF BRUCINE, $C^{23}H^{26}N^2O^4.HCl$, or *Chloride of Brucium*, $C^{23}H^{27}N^2O^4.Cl$ (at 140° C.) A solution of brucine in dilute hydrochloric acid, yields the salt on cooling in crystalline tufts, moderately soluble in water. The *chloromercurate*, $C^{23}H^{26}N^2O^4.HCl.2HgCl$, is obtained as a crystalline magma on mixing the alcoholic solutions of the two component salts; and if the mass be heated with a small quantity of alcohol and strong hydrochloric acid, the liquid on cooling, deposits the double salt in long needles, which must be washed, first with a large quantity of water, and then with strong alcohol.

The *chloroplatinate*, $C^{23}H^{26}N^2O^4.HCl.PtCl^2$, is obtained as a precipitate of a fine yellow colour, by mixing a solution of sulphate of brucine with dichloride of platinum.

HYDROFERROCYANATES OF BRUCINE.—Three of these salts are known: α. $4C^{23}H^{26}N^2O^4.4HCy.2FeCy + 2H^2O$. Precipitated on mixing a solution of ferrocyanide of potassium with nitrate of brucine, in shining needles, sparingly soluble in cold, more soluble in hot water and alcohol; very hygroscopic. When heated to 100° C. or boiled with water, it decomposes, giving off hydrocyanic acid, and depositing a blue precipitate. β. The alcoholic solutions of brucine and hydroferrocyanic acid form a white amorphous precipitate soluble in excess of brucine. It is nearly insoluble in water and in alcohol, has an acid reaction, and is rapidly decomposed by heat. γ. A cold solution of brucine forms with ferricyanide (red prussiate) of potassium, a deep yellow crystalline precipitate, which appears to be more stable than the salt, &c. (Brandes, Ann. Ch. Pharm. lxvi. 266.)

HYDROFLUATE OF BRUCINE.—A solution of brucine in warm, moderately concentrated hydrofluoric acid, deposits, on cooling, small colourless prisms, moderately soluble in water, sparingly in boiling alcohol, nearly insoluble in cold alcohol. Gives off 3·34 per cent. water at 100° C.

Hydriodate of Brucine. $C^{23}H^{26}N^2O^4.HI + aq.$—Rectangular laminæ, or very short prisms; sparingly soluble in cold, more soluble in hot water; dissolves in alcohol more readily than in water. (Regnault.)

Iodate of Brucine.—A solution of brucine in iodic acid, not in excess, yields by evaporation two salts, viz. an acid salt, which crystallises in hard, transparent, four-sided prisms, and an opaque silky salt, which appears to contain an excess of base.

Iodides of Brucine. α. $(C^{23}H^{26}N^2O^4)^2.I^3$.—Orange-yellow precipitate, obtained by adding to a cold alcoholic solution of brucine, a quantity of tincture of iodine not sufficient to form the compound β. (Analysis 33·3 per cent. iodine; calc. 32·4 per cent.)

β. $C^{23}H^{26}N^2O^4.I^3$.—Produced by triturating brucine with excess of iodine, either in powder or in alcoholic tincture. Brown powder soluble in hot alcohol. Treated with a hot dilute acid, it gives off iodine and yields a salt of brucine. With nitrate of silver, it gives a precipitate of iodide of silver. Gave by analysis 36·13 per cent. C; 3·69 H, and 45·66 I; calc. 35·8 C, 3·4 H, and 48·9 I. (Pelletier, Ann. Ch. Phys. [2] xliii. 176.)

Nitrate of Brucine. $C^{23}H^{26}N^2O^4.HNO^3 + 2aq.$—A solution of brucine in dilute nitric acid yields this salt in colourless four-sided prisms, bevelled at the summits. Less soluble in water than nitrate of strychnine.

Oxalate of Brucine crystallises in long needles, especially when the acid is in excess. Sparingly soluble in absolute alcohol.

Perchlorate of Brucine.—Small prisms, sparingly soluble in cold water, more soluble in hot water and in alcohol. Gives off 5·4 per cent. water at 170° C., and explodes at a higher temperature.

Periodate of Brucine crystallises from an alcoholic solution by evaporation at 30° or 40° C. in beautiful colourless needles, which are decomposed by heat with a slight noise. Moderately soluble in water and alcohol; the solutions turn brown when exposed to the air. (Bödeker, Ann. Ch. Pharm. lxxi. 64.—Langlois, Ann. Ch. Phys. [3] xxxiv. 278.)

Phosphates of Brucine. α. $(C^{23}H^{26}N^2O^4)^2.H^3PO^4$, or $(C^{23}H^{27}N^2O^4)^2.H.PO^4$. (at 100° C.)—A solution of brucine in tribasic phosphoric acid yields the salt, when concentrated, in large shortened prisms, having a faint yellowish colour, sparingly soluble in cold water, but dissolving in any proportion in hot water. Neutral to litmus paper. The crystals contain water, which they lose on exposure to the air. At 100° they fuse in their water of crystallisation to a resinous mass, from which it is difficult to expel the last traces of water.—β. *Acid Salt.* Obtained by using an excess of acid. Crystallises in large rectangular plates, very soluble and efflorescent.—γ. *Phosphate of Brucine and Soda* $C^{23}H^{26}N^2O^4.NaH^2PO^4$ (at 100° C.) Obtained by digesting brucine with ordinary phosphate of sodium. Short opaque prisms. (Anderson, Phil. Mag. [3] xxxiii. 163.)

Picrotoxate of Brucine crystallises from a boiling solution in white, silky, flexible needles.

Sulphate of Brucine.—The *normal salt*, $(C^{23}H^{26}N^2O^4)^2.H^2SO^4 + 7aq.$ is obtained by saturating brucine with dilute sulphydric acid. Long needles, very soluble in water, sparingly in alcohol; gives off its water at 130° C. *An acid sulphate* is obtained by crystallising the normal salt with sulphuric acid, and removing the excess of acid by washing with ether.—*Double sulphates.* On adding brucine to a solution of sulphate of copper or iron, part only of the metallic base is precipitated.

Sulphocyanate of Brucine. $C^{23}H^{26}N^2O^4.HCyS$.—Obtained by saturating an alcoholic solution of brucine with a moderately concentrated solution of sulphocyanic acid. Colourless scales, anhydrous, soluble in water, infusible at 100° C.

Tartrates of Brucine. α. *Normal tartrates.* $(C^{23}H^{26}N^2O^4)^2.C^4H^6O^6 + 5\frac{1}{2}aq.$ 8 aq. and 14 aq.—Obtained in limpid well-defined crystals by dissolving 2 at. brucine in a hot aqueous solution of 1 at. tartaric acid. Very soluble in hot, sparingly in cold water.—α. The *tartrate* (dextro-rotatory) is deposited immediately in limpid laminæ, containing 8 at. water, 7½ at. of which are given off at 100° C., and the remainder at 150° (in all 13·22 per cent.; by calculation 13·18 per cent.) Crystallised from 95 per cent. alcohol, the same salt contains only 5½ at. water, or 11 at. water to 2 at. of the salt, 5 of which are given off at 100° C., and the remainder at 150° (in all 10 per cent.; by calculation 9·5 per cent.) The *antitartrate* (lævo-rotatory) always contains $14H^2O$, whether crystallised from water or from strong alcohol. It effloresces quickly in summer; gives off 20·66 per cent. water at 100°, and 1 per cent. more at 150° (in all 21 per cent. = 14 at.)

β. *Acid tartrates.* $C^{23}H^{26}N^2O^4.C^4H^6O^6 + 5aq.$—Obtained by mixing brucine and tartaric acid in equal numbers of atoms. The *tartrate* precipitates immediately and completely, as a granular crystalline powder. It is always anhydrous, whether crystallised from water or from alcohol. Begins to decompose at about 200° C. The *antitartrate* contains 5 at. water (calc. 15·7 per cent.; exp. 14·5 per cent.): gives off 13·3 per cent. (4½ at.) at 100°, the rest at 150°. Very soluble in hot, sparingly in cold water. Effloresces easily in dry air. (Pasteur, Ann. Ch. Phys. [3] xxxviii. 472.)

THIOSULPHATE, OR HYPOSULPHITE OF BRUCINE $(C^{23}H^{26}N^2O^4)^2.H^2S^2O^3 + 5aq.$ (air-dried), is formed when a solution of brucine, mixed with alcohol and sulphide of ammonium, is exposed for some time to the air. It crystallises in prismatic needles, which dissolve in 105 pts. of cold water, and give off 1 at. water when dried over oil of vitriol. (How, Ed. N. Phil. J. [new ser.] vol. xcviii).

Substitution-derivatives of Brucine.

BROMOBRUCINE, $C^{23}H^{25}BrN^2O^4$.—When a solution of bromine in dilute alcohol is added to an aqueous solution of sulphate of brucine, a resinous substance immediately forms: and if the addition of the bromine be continued till two-thirds of the brucine is converted into this substance, the decanted solution then precipitated by ammonia, the precipitate dissolved in very weak alcohol, and boiling water containing a little alcohol poured by small portions into the liquid, and afterwards a little pure water, also boiling, a slight turbidity soon appears; and on leaving the solution to cool, bromobrucine is deposited in small needles, having a slight brown colour. It gave by analysis 17·5 per cent. bromine (calc. 16·9 per cent.) It is not coloured red by strong nitric acid. (Laurent, Ann. Ch. Phys. [3] xxiv. 314.)

ETHYLBRUCINE. $C^{23}H^{25}(C^2H^5)N^2O^4$.—The *hydriodate* of this base is obtained by treating a cooled alcoholic solution of brucine with excess of iodide of ethyl, in crystals containing $2[C^{23}H^{25}(C^2H^5)N^2O^4.HI] + aq.$ insoluble in water, but readily soluble in hot alcohol. Potash does not separate the base from this salt; but on treating the solution with recently precipitated oxide of silver, ethylbrucine [? hydrate of ethylbrucium, $C^{23}H^{25}(C^2H^5)N^2O^4.H.O$, analogous to hydrate of ammonium] is obtained. This base dissolves readily in water, alcohol, and ether, but cannot be obtained in the solid state. The solution has a strong alkaline reaction, precipitates ferric oxide, zinc-oxide, and alumina, redissolving the two latter in excess. It decomposes ammonia-salts, and absorbs carbonic acid from the air. With nitric acid, it gives the same red colour as brucine. It neutralises acids completely. The nitrate and hydrochlorate crystallise, their solutions however becoming coloured during evaporation. The hydrochlorate forms with dichloride of platinum a crystalline double salt, containing $C^{23}H^{25}(C^2H^5)N^2O^4.HCl.PtCl^2$. (Gunning, J. pr. Chem. lxvii. 46.)

BRUCITE. *Nemalite. Lancasterite. Native Magnesia.*—MgHO, the magnesium being sometimes partly replaced by iron. Crystallises in rhombohedral forms. Primary form R = 82° 15′, generally forming the combinations oR . ∞ R. Cleavage very easy parallel to the base. It is usually foliated or massive; also fibrous, the fibres being separable and elastic. Hardness = 1·5. Specific gravity 2·35 (Hardinger). White inclining to grey, blue or green, with pearly lustre. Streak white. Transparent in various degrees, sometimes translucent on the edges only. Sectile. Flexible in thin laminæ. Gives off water when heated, but does not fuse. Dissolves in acids without efflorescence. It accompanies other magnesian minerals in serpentine, in Unst, one of the Shetland isles, where it is sometimes found in regular crystals; at Pyschminsk in the Ural; at Goujat in France; at Hoboken New Jersey; and in the State of New York. (Dana, ii. 133.)

The name *Brucite* is also used as a synonyme of CHONDRODITE (*q. v.*)

BRUNOLIC ACID. A substance obtained by Runge from coal-tar naphtha (Pogg. Ann. xxi. 65, 315; xxxii. 308). When the alkaline liquid obtained by treating coal-tar naphtha with milk of lime, is mixed with an acid, a mixture of phenic or carbolic acid, rosolic acid and brunolic acid separates out; and on distilling this mixture with water, the phenic acid passes over, leaving a brown pitchy residue, containing rosolic and brunolic acid. When this mixture is dissolved in a small quantity of alcohol, and milk of lime added, a rose-coloured solution is formed, containing rosolate of calcium, while brunolate of calcium separates as a brown precipitate, which when decomposed by hydrochloric acid, yields brunolic acid in brown flakes. It appears to combine with bases, but neither the acid itself nor any of its salts have yet been obtained in a definite state.

BRUNSWICK-GREEN. A green pigment consisting of oxychloride of copper, $Cu^8Cl^2O^3 = 2CuCl.3Cu^2O$, prepared by moistening copper turnings with hydrochloric acid or solution of sal-ammoniac, and leaving them in contact with the air. The oxychloride then forms on the surface, and is washed off with water, and dried at a gentle heat. (See COPPER.)

BRYOIDIN. One of the constituents of the resin of arbol-a-brea (p. 354).

BRYONIN. The bitter principle of the root of the red-berried bryony (*Bryonia dioica*). It may be obtained by treating the root with boiling water, precipitating the filtered liquid with subacetate of lead, decomposing the precipitate with sulphuretted hydrogen, evaporating the filtered liquid, and exhausting the residue with alcohol (Brandes and Firnhaber, Brandes' Arch. Pharm. iii. 356). It is a yellowish-white mass, sometimes red or brownish; tastes sweetish at first, then styptic and very bitter. Soluble in water and alcohol, insoluble in ether. Sulphuric acid dissolves it, forming a blue liquid, which changes to green. It is not altered by alkalis. The aqueous solution forms white precipitates with nitrate of silver, mercurous nitrate, and subacetate of lead. Bryonin acts as a drastic purgative, and in large doses is poisonous. (Gerh. Traité, iv. 274.)

According to Walz (Chem. Centralb. 1859, p. 5), the alcoholic extract of bryony root contains two bitter substances, bryonin and bryonitin, which may be separated by treating the aqueous infusion of the alcoholic extract with subacetate of lead, which precipitates the greater part of the bryonitin, leaving bryonin in solution. *Bryonin*, when freed from adhering resin by treatment with absolute ether, is a white or slightly coloured granular substance, transparent in thin layers, and according to Walz, contains $C^{48}H^{80}O^{19}$; but the simpler formula, $C^{5}H^{8}O^{2}$, agrees well enough with the results of the analysis. It appears to be a glucoside, and is resolved by boiling with dilute sulphuric acid, into glucose, and two amorphous bodies, viz. bryoretin, soluble in ether, and hydrobryoretin, insoluble in ether, but soluble in alcohol:

$$\underset{\text{Bryonin.}}{C^{48}H^{84}O^{21}} = \underset{\text{Bryoretin.}}{C^{21}H^{35}O^{7}} + \underset{\text{Hydro-bryoretin.}}{C^{21}H^{37}O^{8}} + \underset{\text{Glucose.}}{C^{6}H^{12}O^{6}}$$

Bryonitin forms a white crystalline mass, soluble in water and ether, insoluble in alcohol. Walz regards the bryonin of Brandes and Firnhaber as an impure substance.

BRYORETIN. See the last article.

BUBULIN (from βοὸς, ox). The name of a peculiar substance, said by Morin to exist in cow-dung, and to be copiously precipitated by metallic salts, tincture of galls, and alum, and therefore to be active in the application of cow-dung to calico-printing.

BUCHOLZITE. A silicate of aluminium, varying in composition between $Al^{4}O^{3}.SiO^{2}$ and $2Al^{4}O^{3}.3SiO^{2}$, and probably nothing but fibrous disthene mixed with quartz. (See DISTHENE and SILLIMANITE.)

BUCKLANDITE. See EPIDOTE.

BUCKTHORN. See RHAMNUS.

BUCKWHEAT. *Polygonum fagopyrum*, and *P. tartaricum*.—A plant indigenous in Asia, but much cultivated in the North of Europe, where the flour is used for food. The dry plant yields on the average, 43 per cent. by weight of grain, and 57 straw.

The seed of buckwheat contains on the average:

	Air dried.	Anhydrous.
Nitrogenous matter	8·6	10·0
Starch, &c.	51·9	60·5
Woody fibre, &c.	23·1	26·9
Ash	2·2	2·5
Water	14·2	

Pierre (Compt. rend. xlvi. 203) found in 100 pts. of buckwheat-seed, 2·1 pts. nitrogen, 0·5 phosphoric anhydride, and 3·2 fat; in 100 pts. of commercial buckwheat flour: 1·3 pts. nitrogen; in 100 pts. of the coarse yellow flour: 5·6 nitrogen, 2·4 phosphoric anhydride, and 7·2 fat; in the bran, 2·4 nitrogen, 1·2 phosphoric anhydride, and 4·8 fat. Mulder found in 100 pts. of buckwheat flour 7·5 pts. nitrogenous constituents, and the same in the bran.

Composition of the Ash of the Grain and Straw of Buckwheat.

	Grain.			Straw.					
	1	2	3	4	5	6	7	8	9
Potash	8·7	15·0	10·3	31·7	21·6	39·6	40·5	28·2	23·9
Soda	20·1	24·0	—	—	—	—	—	—	—
Lime	6·7	11·5	22·0	15·7	14·0	12·8	11·6	14·1	18·6
Magnesia	10·4	13·5	40·3	1·6	1·9	3·2	1·4	4·7	4·2
Ferric oxide	1·0	0·6	0·5	—	—	—	—	—	—
Sulphuric anhydride	2·2	5·4	6·8	4·7	2·8	2·7	4·3	7·1	3·5
Silicic „	0·7	10·6	4·4	3·6	4·1	4·1	4·2	4·8	5·2
Phosphoric „	50·1	12·5	9·0	10·3	9·5	6·4	8·9	10·9	10·0
Chloride of potassium	—	—	—	7·4	26·9	0·8	3·1	6·8	9·7
Chloride of sodium	—	1·0	4·9	4·5	3·0	3·2	3·7	3·4	1·7
Carbonic anhydride	—	—	—	20·4	16·1	27·1	22·2	20·0	23·1
Alumina	—	1·9	0·8	—	—	—	—	—	—
Manganic oxide	—	3·2	1·0	—	—	—	—	—	—

1. Analysed by Bichon (Ann. Ch. Pharm. l. 419). 2, 3. By Sprengel (J. techn. Chem. vi. 402; x. 350). 4—9. By Wolff (J. pr. Chem. lii. 65). 4. Straw of buckwheat grown in unmanured soil; 5, on soil manured with chloride of sodium; 6. with nitrate of potassium; 7, with potashes; 8, with sulphate of magnesium; 9, with lime.

Sprengel found in the air-dried straw, 3·20 per cent. ash.

Colouring Matters of Buckwheat.—The leaves contain a yellow colouring-matter, first observed by Nachtigal (Jahresber. f. Chem. 1849, p. 713), further examined by Schunck (Chem. Gaz. 1858, Jan. 18; Jahresber. 1857, p. 489). According to Schunck, its composition may be most simply expressed by the formula, $C^3H^4O^2$, and it is probably identical with *rutin* (*q. v.*), and with Moldenhauer's *ilixanthin.* It crystallises in yellow needles, dissolves sparingly in cold water, more readily in boiling water, more still in alcohol. Alkalis dissolve it, forming a deep yellow solution, from which it is precipitated by acids; if, however, the solution be exposed to the air, the colouring matter is transformed into an amorphous substance, easily soluble in water, and no longer precipitable by acids. Hydrochloric and sulphuric acids change the yellow colour of the crystalline substance to deep orange: but water restores it. Dilute sulphuric acid does not decompose it, even at boiling heat; nitric acid converts it into oxalic acid. With oxide of lead, it forms a bright yellow compound, like chromate of lead, and communicates a bright yellow colour to cotton stuffs mordanted with acetate of alumina. The presence of foreign matters in the crude extract of buckwheat straw, renders the colour somewhat impure. According to Nachtigal, 5 pts. of buckwheat straw contain as much colouring matter as 1 pt. of quercitron. According to Schunck, 1000 pts. of the fresh leaves contain rather more than 1 pt. of pure colouring matter.

Buckwheat straw has been said to yield indigo by fermentation; a statement which, however, is not confirmed by the observation of Schunck (Handw. d. Chem. 2te Aufl. ii. [2] 551. *Ure's Dictionary of Arts, Manufactures, and Mines*, ii. 467.)

BUCURUMANGA RESIN. A fossil resin, occurring in an auriferous alluvium near Bucurumanga in New Granada. It is light yellow, transparent, somewhat heavier than water; becomes strongly electric by friction; is insoluble in alcohol; swells up in ether and becomes opaque. It melts when heated, and burns in the air without residue. It resembles amber in outward appearance, but does not yield succinic acid by dry distillation. It contains 82·7 per cent. carbon, 10·8 hydrogen, and 6·5 oxygen. (Boussingault, Ann. Ch. Phys. [3] vi. 507.)

BUENIN. A substance obtained by Buchner, from the bark of *Buena hexandra.*

BUHRSTONE. A cellular flinty quartz rock.

BUKKU LEAVES. The leaves of *Diosma crenata*, a rutaceous plant growing at the Cape of Good Hope. Gassincourt (Buchn. Répert. Pharm. xxvi. 328) found in 1000 pts. of them, besides gum, resin, &c., 6·6 pts. of a volatile oil, having a gold-yellow colour, a sharp irritating taste and odour, lighter than water, and somewhat soluble therein. Brandes (Arch. d. N. Apoth. Ver. xxii. 229) found malic and oxalic acids in the leaves, besides albumin, gum, resins, &c.; and in 1000 pts. 88 pts. volatile oil, and 40 pts. of a yellowish-brown bitter substance, soluble in water, which he called *diosmin.* Landerer (Buchner's Répert. lxxxiv. 63) found in the alcoholic tincture of bukku leaves, a crystalline bitter deposit, which, however, was insoluble in water.

BURATITE. A hydrated carbonate of zinc, copper, and calcium, occurring in verdigris-green, radiated, acicular crystals, or plumose aggregations, of specific gravity 3·32, at Chessy and Frammont in France, and at Volterra and Temperino in Tuscany (Delesse, Ann. Ch. Phys. [3] xviii. 478). It is very variable in composition, and is probably a mixture of several minerals.

BURETTE. See Analysis, Volumetric (p. 256).

BURGUNDY PITCH or **RESIN.** *Poix de Bourgogne, Pix alba, Poix blanche*, is the white pitch obtained from pine-wood. The resin of *Pinus picea* purified by repeated boiling with water, is also called *Burgundy pitch.* (See Pine-resins and Pitch.)

BURSERA GUMMIFERA. *Gommart.*—A terebinthaceous tree growing in the Antilles. It yields a dry white resin having a crystalline fracture, and an odour of turpentine, also like that of elemi. It is but slightly fusible, but diffuses itself through boiling water in small tenacious granules. The resin distilled with water yields 47 per cent. of a coloured volatile oil (*Gommart-oil, Essence de gommart*), which, when purified by standing in contact with potash, then with potassium, and rectification, has the same odour, composition, and vapour-density as oil of turpentine, and forms with hydrochloric acid, two compounds, one of which is crystalline and consists of $C^{10}H^{16}.2HCl$. (H. Deville, Ann. Ch. Phys. [3] xxvii. 90.)

BUSTAMITE. Native silicate of manganese. See Rhodonite.

BUTEA GUM. *Bengal Kino.*—The juice of *Butea frondosa*, Roxb., often sent into the market instead of genuine kino. It forms black-brown, slightly lustrous, brittle lumps, has an astringent taste, and yields pyrocatechin by dry distillation.

BUTIC ACID. A solid fatty acid, which Heintz obtained (Pogg. Ann. xc. 137), though not pure, by partially precipitating an alcoholic solution of the solid fatty acids of butter with acetate of magnesium, this acid then forming the less soluble compound. Heintz is of opinion that in the pure state it would have the composition of arachidic acid $C^{20}H^{40}O^2$. (See p. 353.)

BUTTER. The fatty non-azotised constituent of milk. It is suspended in the milk in minute globules, and rises to the surface, when the milk is left at rest, in the form of cream, together with a certain quantity of casein and the other constituents of the milk. Butter is obtained from cream by agitation or *churning*, which causes the fat-globules to unite in larger masses and separate completely from the watery liquid, called *butter-milk*. Butter thus obtained and in the state in which it is commonly used, consists of $\frac{5}{6}$ pure fat or real butter and $\frac{1}{6}$ of butter-milk, from which it may be separated by melting it in a tall vessel at about 60° C., decanting the clear fat which floats at the top, and washing with water at 40° C. Ordinary butter from cow's milk, is composed, according to Chevreul, of stearin, margarin, and olein, with small quantities of butyrin, caproin, and caprin, to which its odour is due. According to Heintz, it contains olein, a large quantity of palmitin, and a small quantity of stearin, together with very small quantities of glycerides, yielding by saponification, myristic acid and *butic acid*, $C^{20}H^{10}O^2$ (*vid. sup.*)

Butter dissolves in 28 pts. of boiling alcohol of specific gravity 0·82. It is very apt to turn rancid, a change which consists in the separation of the fatty acids from the glycerin, and may be prevented to a certain extent by salting or by melting it, so as to separate the foreign matters which induce the decomposition.

"At Constantinople, the butter brought from the Crimea and the Kirban, is kept sweet by melting it while fresh over a very slow fire, and removing the scum as it rises. By melting butter in this manner, and then salting it, it may be kept good and fine-tasted for two years; moreover, this melting, if carefully done, injures neither the taste nor colour. Thénard too recommends the same method. He directs the the melting to be done on a water-bath, or at a heat not exceeding 140° Fahr.; and to be continued till all the caseous matter has subsided to the bottom, and the butter is transparent. It is then to be decanted, or strained through a cloth, and cooled in a mixture of pounded ice and salt, or at least in cold spring water, othewise it will become lumpy by crystallising, and likewise not resist the action of the air so well. Kept in a close vessel, and in a cool place, it will thus remain six months or more, nearly as good as at first, particularly after the top is taken off. If beaten up with one-sixth of its weight of the cheesy matter when used, it will in some degree resemble fresh butter in appearance. The taste of rancid butter, he adds, may be much corrected by melting and cooling in this manner.

"Another mode of curing butter, is as follows: Take one part of sugar, one of nitre, and two of the best Spanish great salt, and rub them together into a fine powder. This composition is to be mixed thoroughly with the butter, as soon as it is completely freed from the milk, in the proportion of one ounce to sixteen; and the butter thus prepared is to be pressed tight into the vessel prepared for it, so as to leave no vacuities. This butter does not taste well, till it has stood at least a fortnight: it then has a rich marrow flavour, that no butter ever acquires; and with proper care may be kept for years in this climate, or carried to the East Indies, if packed so as not to melt.

"At Kebba, in the interior of Africa, Mungo Park informs us, there is a tree much resembling the American oak, producing a nut in appearance somewhat like an olive. The kernel of this nut, by boiling in water, affords a kind of butter, which is whiter, firmer, and of a richer flavour than any he ever tasted made from cows' milk, and will keep without salt the whole year. The natives call it *shea toulou*, or tree butter. Large quantities of it are made every season." U.

Butter is often largely adulterated with water and salt, which are introduced while the butter is in the melted state and incorporated by stirring till the whole is cold. The proportion of water may be determined very nearly by melting a portion of the butter in a narrow glass vessel, such as a common ounce phial, and leaving it to stand in a warm place till the water settles to the bottom. The quantity of the water should not exceed 1 per cent. The amount of salt is determined by calcination, any quantity beyond 5 per cent. may be regarded as adulteration. Butter is also frequently adulterated with lard, in places where that kind of fat is cheap. (For the preparation of butter, see *Ure's Dictionary of Arts, Manufactures, and Mines*, also *Muspratt's Chemistry*, i. 397.)

BUTTER OF ANTIMONY, TIN, &c. Old names for anhydrous metallic chlorides having a buttery consistence.

BUTYL and derivatives. Syn. TETRYL and derivatives.

BUTYLACTIC ACID. *Oxybutyric acid.* $C^4H^8O^3 = (C^4H^6O)''.H^2.O^2$. (A. Wurtz, Ann. Ch. Pharm. cvii. 197.)—This acid has hitherto been obtained only by the oxidation of amyl-glycol (p. 208); but it might doubtless be produced also by the oxidation of butyl-glycol, as well as by other processes. It is prepared by gently heating 14 pts. of amyl-glycol with 30 pts. nitric acid (HNO^3) and 42 pts. water, and evaporating over quick lime; it then remains in the form of a syrupy liquid.

Butylactic acid bears to butyric acid the same relation that lactic acid bears to propionic acid, and in consequence of this relation, it is regarded as dibasic (see LACTIC ACID), although all the salts yet obtained from it contain but one atom of metal in place of hydrogen. The *barium-salt*, $C^4H^7BaO^3$, is uncrystallisable, dissolves in all proportions, and with moderate facility, in dilute alcohol, but is insoluble in absolute alcohol; ether precipitates it from the alcoholic solution. The *calcium-salt*, $C^4H^7CaO^3$ (dried at 120° C.), separates from the aqueous solution by spontaneous evaporation in warty crystals, which dissolve readily in water and in absolute alcohol, but are insoluble in ether. The *zinc-salt*, $C^4H^7ZnO^3 + aq.$, crystallises in shining laminæ, which dissolve in 160 pts. of water at 15° C., but are insoluble in absolute alcohol. The crystals are permanent in the air, but give off 11 per cent. (2 at.) water at 100° C.

BUTYRACETIC ACID. *Pseudo-acetic Acid.* $C^3H^6O^2$ or $C^2H^4O^2.C^4H^8O^2$.—An acid first obtained by Nöllner in 1841 (Ann. Ch. Pharm. xxxviii. 229), as a product of the fermentation of a mother-liquor from the preparation of tartaric acid containing a considerable quantity of tartrate of calcium, or by converting crude tartar into impure tartrate of calcium, and fermenting the product. Nöllner designated this acid *pseudo-acetic acid*, from its resemblance to acetic acid. Berzelius regarded it as a mixture of acetic and butyric acids. Nicklès, however (Compt. rend. xxxiii. 419), showed that, although this acid is easily resolved into acetic and butyric acids, it is, nevertheless a distinct acid, and gave it the name butyracetic acid. Dumas, Malaguti, and Leblanc (Compt. rend. xxv. 781), showed that it is identical in composition and boiling point with propionic acid, which it also resembles in its other physical properties, and moreover stated that its salts are identical with the propionates in composition and crystalline form. Nicklès, on the other hand, maintained that the salts differ in certain respects from the corresponding propionates. Lastly, the acid has been examined by Limpricht and v. Uslar (Ann. Ch. Pharm. xciv. 321), who have shown that butyracetate of barium yields, by dry distillation, propylal, propione, and propylene (tritylene), in which respect it exactly resembles the propionate, but that, on the other hand, butyracetic acid separates spontaneously or by distillation, into acetic and butyric acids, which is *not* the case with propionic acid. On the whole, therefore, butyracetic acid must be regarded as a distinct acid. It appears to be produced only by the fermentation of tartrate of calcium; acid tartrate of potassium, whether crude or purified, yields by fermentation nothing but acetic acid. According to later experiments of Nicklès (J. Pharm. [3] xxxiii. 351), it is likewise obtained by pouring a mixed solution of equivalent qualities of an acetate and a butyrate into dilute sulphuric acid.

Butyracetic acid resembles propionic acid in most of its properties. It mixes in all proportions with water, and is separated therefrom unaltered by chloride of calcium, a property which distinguishes it from a mere mixture of butyric and acetic acids. According to Dumas, it boils constantly at 140° C.; but, according to Limpricht and v. Uslar, it begins to boil at 120°, at which temperature nearly pure acetic acid passes over, and the boiling point gradually rises to 160°, when butyric acid distils over, the boiling point not remaining stationary for any time at 140°. It does not yield either a definite anhydride or a definite ether, but in both cases a mixture of acetate and butyrate.

Butyracetate of Barium, $C^3H^5BaO^2 + \frac{1}{2}aq.$, resembles the propionate in composition and properties; but on decomposing it with sulphate of copper, the acid which is set free separates into butyric and acetic acids (Nicklès). The *calcium-salt*, $C^3H^5CaO^2$, forms silky needles, or, according to Nicklès, regular octahedrons, which effloresce in the air. The *copper-salt* crystallises in dark blue-green tables, which give off part of their water of crystallisation at 100° C. It rotates on water, dissolves sparingly in water, more easily in alcohol.

The *neutral lead-salt* crystallises from a very concentrated solution at low temperatures in cauliflower-like masses. It melts when heated, giving off part of its acid, and deliquesces in moist air. A concentrated solution, to which chloride of barium is added as long as the precipitate first formed disappears on agitation, yields by slow evaporation, a double salt which crystallises in square prisms containing barium and lead, and likewise chlorine. The *basic lead-salt* is formed by boiling the preceding with oxide of lead. It crystallises from a moderately concentrated solution at a little above 0° C., in octahedrons which contain 42 per cent. water, undergo aqueous fusion below 19°, and dissolve readily in alcohol. From a very concentrated solution or from fusion, it crystallises in tables; at very low temperatures, however, in spherical segments, which, when gently heated, split from the centre outwards with a slight noise. By mixing the boiling solution of the lead-salt with a little ammonia, a crystalline powder is precipitated. (Nöllner.)

The *mercurous salt* crystallises in satiny scales, which are reddened by light. The *potassium-salt* crystallises in very deliquescent thin tables. The *silver-salt* separates on cooling from a boiling solution of the ammonium-salt, mixed with a boiling solution of nitrate of silver, in shining needles resembling acetate of silver and sparingly soluble in water. The *sodium-salt* crystallises from a somewhat dilute solution in deliquescent octahedrons; from a more concentrated solution, as a white tallowy amorphous mass, or as a radio-crystalline mass. The *zinc-salt* is soluble in water, but decomposes by boiling.

BUTYRAL and BUTYRALDEHYDE, C^4H^8O. — Two compounds are known which have the composition of the term in the butyric series corresponding to that of aldehyde in the acetic series; they are not, however, identical.

Butyral was obtained by Chancel (Ann. Ch. Phys. [3] xii. 416), among the products of the destructive distillation of butyrate of calcium. The crude product of this operation is a mixture of several substances, of which butyral, boiling at 95° C. is the most volatile, and can be separated from the others by fractional distillation.

Pure butyral is a colourless, very mobile liquid, with a burning taste, and a sharp and penetrating odour. Its density at 22° C. is 0·821, and it boils at 95°. It dissolves a small quantity of water. It is slightly soluble in water, and soluble in all proportions in alcohol, ether, and wood-spirit. It rapidly absorbs oxygen from the atmosphere, and is converted into butyric acid. It is oxidised by solid chromic acid with a slight explosion. It is very inflammable and burns with a brilliant flame. Heated with water and oxide of silver, it reduces part of the oxide to the state of metallic silver, butyrate of silver remaining in solution. On heating it with sulphuric acid, sulphurous acid is liberated, and a small quantity of butyric acid remains in solution. By dilute nitric acid, it is converted into nitropropionic acid. It forms crystalline compounds with acid sulphites of alkali-metals, analogous to those which aldehyde forms. By the action of pentachloride of phosphorus on butyral, hydrochloric acid, oxychloride of phosphorus, and a peculiar product, C^4H^7Cl, are formed:

$$C^4H^8O + PCl^5 = C^4H^7Cl + HCl + POCl^3.$$

This product is a colourless, oily, very mobile liquid, lighter than water, with a sharp odour and a biting taste. It is insoluble in water, but soluble in alcohol and in ether. It boils at a little over 100° C.; it is inflammable, and burns with a green-edged flame. It is probable that the action of pentachloride of phosphorus on butyral is analogous to its action on aldehyde, and gives rise to the compound $C^4H^8Cl^2$, homologous with chloride of ethylidene (p. 107), and that at the moment of its formation, this substance is decomposed into hydrochloric acid and the body above described.

Chlorinated Derivatives of Butyral. — Chlorine acts very energetically on butyral, with the formation of definite compounds containing chlorine in the place of hydrogen.

Monochlorinated Butyral. C^4H^7ClO.—Produced by passing a current of dry chlorine through butyral by diffused light. The gas is at first absorbed, with evolution of heat and pale red coloration; afterwards the colour disappears and the liquid gives off torrents of hydrochloric acid gas to the end of the operation. A rapid current of carbonic anhydride is then passed through the liquid heated somewhat below its boiling point, and it is then rectified. It is a transparent limpid liquid, heavier than water; boils at 141° C.; has a pungent tear-exciting odour. It is insoluble in water, but dissolves in alcohol, and its alcoholic solution does not cloud nitrate of silver. It does not form an amide with ammonia.

Dichlorinated Butyral, $C^4H^6Cl^2O$.—When dry chlorine is passed for three hours through butyral exposed to sunlight, the action is observed to slacken after some time. If carbonic anhydride be now passed through the liquid, which is afterwards rectified, a neutral oil is obtained boiling at 200° C.

Tetrachlorinated Butyral, $C^4H^4Cl^4O$. — Chlorine is passed for several days through butyral exposed to bright sunshine, the liquid being ultimately heated, and the action continued as long as hydrochloric acid gas continues to be evolved. When purified like the other substances, it forms a thick heavy neutral oil, which boils at a high temperature, with decomposition.

Butyraldehyde. $C^4H^8O = C^4H^7O.H$.—This body was obtained by Guckelberger among the products of the action of oxidising agents on fibrin, albumin, and casein.

For the full details of the process, Guckelberger's paper must be referred to (Ann. Ch. Pharm. lxiv. 39). The crude distillate resulting from the action was neutralised with chalk and distilled. A neutral distillate was obtained which consisted of the aldehydes of the acetic, propionic, butyric, and benzoic series. These were separated by fractional rectification, the portions between 70° and 100° C. which consisted of butyric aldehyde mixed with a little propionic aldehyde, being collected separately. Butyric aldehyde is much less soluble in water than propionic aldehyde, and may be separated from it by agitation with water. To obtain the butyraldehyde quite pure, it is agitated with ammonia, with which it forms a crystalline compound. This is decomposed by the addition of a concentrated solution of alum, the liquid distilled, and the distillate rectified over chloride of calcium.

When pure, it is a thin, colourless, transparent oil, which has the specific gravity 0·80 at 15° C. It boils at 68° to 75°, and has an ethereal, somewhat penetrating odour. The small quantity in which this substance has been found, has prevented its complete investigation; but almost all its properties, as far as they have been examined, are identical with those of butyral. It acidifies in the air; an aqueous solution mixed with ammonia, and then with nitrate of silver until the alkaline reaction disappears, gives, on the application of heat, a beautiful coating of metallic silver on the sides of the vessel. It differs from its isomer chiefly in its boiling point, its density, and in forming a crystalline compound with ammonia, which butyral does not.

Butyraldehyde-ammonia. $NH^3.C^4H^8O + 5aq.$ — Butyraldehyde forms with strong ammonia, a crystalline mass consisting of small acute rhombic octahedrons; from an alcoholic solution, the compound crystallises in large rhombic tables. The dry crystals do not alter in the air, but in the moist state they gradually become brown. Gently heated, they melt, and sublime at a few degrees above 100° C.; more strongly heated, they give off ammonia. Potash does not expel ammonia from them at ordinary temperatures. Aqueous acids or alum separate butyraldehyde. Butyraldehyde-ammonia is almost insoluble in water, but soluble in alcohol, and in ether.

Sulphuretted hydrogen passed into a solution of this body, appears to form a compound homologous with thialdine. When the liquid resulting from this action is treated with ether, a sulphuretted oil is obtained, which forms with hydrochloric acid a solid crystalline compound.

E. A.

BUTYRAMIDE. $C^4H^9NO = \left.\begin{matrix}C^4H^7O\\H^2\end{matrix}\right\}N.$ This compound, homologous with acetamide, is prepared by placing 1 pt. of butyric ether, and 6 pts. of strong aqueous ammonia, in a flask, and frequently agitating the mixture until the action is complete, which generally takes from eight to ten days: the liquid is then evaporated to one-third, and on cooling the butyramide crystallises out:

$$\underset{\text{Butyric ether.}}{C^4H^7(C^2H^5)O^2} + NH^3 = \underset{\text{Butyramide.}}{C^4H^9NO} + \underset{\text{Alcohol.}}{C^2H^6O}$$

It crystallises in snow-white, nacreous, transparent tables, which melt at 115° C. to a colourless liquid, and volatilise without residue. It has a sweet, cooling taste, with bitter aftertaste. It is readily soluble in water, also in ether and in alcohol. Its vapour is inflammable. Passed over red-hot lime, or distilled with anhydrous phosphoric acid, it loses water and yields butyronitrile (cyanide of trityl):

$$\underset{\text{Butyramide.}}{C^4H^9NO} - H^2O = \underset{\text{Butyronitrile.}}{C^4H^7N}$$

Its aqueous solution is decomposed by boiling with fixed alkalis, yielding ammonia and an alkaline butyrate:

$$C^4H^9NO + KHO = C^4H^7KO^2 + NH^3.$$

By pentachloride of phosphorus, it is converted into cyanide of trityl, oxychloride of phosphorus, and hydrochloric acid:

$$C^4H^9NO + PCl^5 = C^4H^7N + POCl^3 + 2HCl.$$

It is decomposed by nitrous acid, with formation of butyric acid, water, and nitrogen:

$$\underset{\text{Butyramide.}}{C^4H^9NO} + \underset{\text{Nitrous acid.}}{HNO^2} = \underset{\text{Butyric acid.}}{C^4H^8O^2} + H^2O + N^2$$

Mercuric Butyramide. C^4H^8HgNO, is obtained by boiling mercuric oxide with solution of butyramide. The filtered solution, when concentrated, deposits the compound in small nacreous crystals, more lustrous than butyramide, which they otherwise resemble.

E. A.

BUTYRIC ACID. $C^4H^8O^2 = \left.\begin{matrix}C^4H^7O\\H\end{matrix}\right\}O.$—Butyric acid is a member of the series of volatile fatty acids, of the general formula $C^nH^{2n}O^2$. It was discovered by Chevreul, who obtained it by saponifying butter with alkalis. It occurs in nature both in the free state, and in combination with bases. It is found in perspiration, in the juice expressed from human flesh, and from that of animals; in crude oil of amber; and in cod-liver oil. It is found in all liquids containing lactic acid, as a product of the transformation of this substance. Butyric acid is also contained, together with several fatty acids of the same series, in combination with glycerin, in butter from cows and goat's milk. This compound of butyric acid with glycerin is inodorous, and it is to its decomposition on standing, by which butyric acid is set free, that the odour of rancid butter is chiefly due. Butyric acid is a frequent product of the oxidation of organic substances, as when fibrin is treated with sulphuric acid and peroxide of manganese, or when oleic acid is oxidised by nitric acid. It has also been found among the products of the destructive distillation of tobacco (Zeise) and of peat (Sullivan, Jahresber. d. Chem. 1858, 280). Lastly, it has been found in several plants, in certain beetles, and in certain mineral waters. (Gm. x. 76; xiii. 388; Handw. d. Chem. ii. [2] 561.)

The most important mode of its formation, and that on which the present methods used for its preparation are based, depends on the metamorphosis which starch, sugar, &c. undergo in the presence of substances which act as ferments. Pelouze and Gélis have found that butyric acid can be obtained from all amylaceous and saccharine matters, which can be transformed into lactic acid, such as cane-sugar, milk-sugar, starch, dextrin, &c. These substances exposed in water to a temperature of 25° to 30° C. in contact with old cheese, or some other decaying nitrogenous substance, first undergo the lactic fermentation, and are ultimately converted into butyric acid. This latter phase is attended with disengagement of carbonic anhydride and hydrogen:

$$\underset{\text{Lactic acid.}}{C^6H^{12}O^6} = \underset{\text{Butyric acid.}}{C^4H^8O^2} + 2CO^2 + H^4.$$

The original process given by Pelouze and Gélis, has subsequently been modified by Bensch, whose method is essentially as follows: 6 lbs. of cane-sugar and ½ an oz of tartaric acid are dissolved in 26 lbs. of boiling water, and left to stand for some days to allow the cane-sugar to pass into grape-sugar. To this solution, about 4 oz. of decayed cheese, diffused in 8 lbs. of sour skim-milk, together with 3 lbs. of chalk, are added, and the whole is left in a place the temperature of which is uniform at about 30—35° C. The mixture is frequently stirred, and generally solidifies after ten or twelve days, to a thick mass of lactate of calcium. If this be allowed to stand under the same conditions, the evaporated water being renewed, it again becomes liquid, gas bubbles rise, and at the expiration of five to six weeks, when the disengagement of gas has ceased, the whole of the lactic acid (and therefore the whole of the sugar), has passed into butyric acid, which is present as butyrate of calcium. The operation seems to succeed best with large quantities of substance.

The above solution of butyrate of calcium is mixed with an equal bulk of water, and a solution of eight pounds of crystallised soda is added, with agitation. The solution filtered off from the carbonate of calcium is evaporated to ten pounds, and decomposed by the careful addition of five and a half pounds of sulphuric acid, previously diluted with an equal weight of water. The greater part of the butyric acid then separates as an oily layer on the surface of the solution of the acid sulphate of sodium, and is removed by means of a tap-funnel. In order to obtain the butyric acid still contained in the solution of sulphate of sodium, it is distilled, the distillate neutralised with carbonate of sodium, evaporated, and the acid separated as before by means of sulphuric acid.

The united portions of crude butyric acid, which, besides water, always contain some sulphate of sodium, are mixed with sulphuric acid (about one ounce to one pound) in order to prevent the separation of neutral sulphate of sodium, which would cause convulsive distillation. The distillate consisting of aqueous butyric acid is mixed with fused chloride of calcium, and rectified. At first, dilute acid passes over accompanied by traces of hydrochloric acid; this afterwards gives place to concentrated acid, which when fractionally distilled, is obtained of a constant boiling point and quite pure. It is better to use sulphuric than hydrochloric acid in the decomposition of butyrate of calcium, as the latter causes the mixture to froth up, and it is difficult to free the butyric acid completely from hydrochloric acid.

Butyric acid may also be prepared by saponifying butter with an alkali, and distilling the soap with sulphuric acid. But this method is never used for the preparation of *pure* butyric acid, as its separation from the accompanying soluble fatty acids is very difficult and troublesome.

Properties.—Butyric acid, when pure, is a colourless, transparent, and very mobile liquid, having an odour suggestive both of vinegar and of rancid butter. It has a very sour and burning taste, and attacks the skin like the strongest acids. It boils at

157° C. under 760 mm. pressure (Kopp), and distils without alteration. Its vapour-density varies with the temperature; at 261° C. it was found to be 3·7, corresponding to 2 vols. The vapour is inflammable, and burns with a blue flame. The density of the liquid acid is 0·9886 at 0° C.; 0·9739 at 15°; and 0·9675 at 25°. It does not solidify at 20°, but in a mixture of solid carbonic acid and ether it crystallises in plates. Butyric acid is soluble in all proportions in water, alcohol, and wood-spirit.

Decompositions.—1. Butyric acid dissolves in *sulphuric acid* without alteration in the cold; at higher temperatures, the greater part distils off unchanged.—2. It also dissolves in *nitric acid* in the cold; by prolonged ebullition with nitric acid of specific gravity 1·40, it is transformed into succinic acid:

$$\underset{\text{Butyric acid.}}{C^4H^8O^2} + O^2 = \underset{\text{Succinic acid.}}{C^4H^6O^4} + H^2O.$$

3. *Iodic acid* does not act upon butyric acid.—4. Butyric acid is energetically attacked by *chlorine*, with formation of hydrochloric acid and of dichlorobutyric acid, $C^4H^6Cl^2O^2$. If the action of the chlorine be continued, the butyric acid is ultimately converted into tetrachlorobutyric acid, $C^4H^4Cl^4O^2$. *Iodine* has scarcely any action on butyric acid.—5. By the action of *pentachloride of phosphorus*, chloride of butyryl, C^4H^7OCl, oxychloride of phosphorus, and hydrochloric acid are formed:

$$\underset{\text{Butyric acid.}}{C^4H^8O^2} + PCl^5 = \underset{\text{Chloride of butyryl.}}{C^4H^7OCl} + POCl^3 + HCl.$$

6. With *pentasulphide of phosphorus*, it forms thiobutyric acid (p. 694).

$$\underset{\text{Butyric acid.}}{5\left(\left.\begin{matrix}C^4H^7O\\H\end{matrix}\right\}O\right)} + P^2S^5 = \underset{\text{Thiobutyric acid.}}{5\left(\left.\begin{matrix}C^4H^7O\\H\end{matrix}\right\}S\right)} + P^2O^5.$$

BUTYRATES.—Butyric acid is monobasic, the butyrates being represented by the general formula $C^4H^7MO^2 = C^4H^7O.M.O.$

When quite dry, they are inodorous; but when moist, they possess a strong odour of butter. They are mostly soluble in water, and crystallisable. Many of them rotate when thrown upon water.

Butyrate of Ammonium, $C^4H^7(NH^4)O^2$.—A deliquescent salt, which gives butyronitrile, C^4H^7N, when distilled with anhydrous phosphoric acid.

Butyrate of Allyl. }
Butyrate of Amyl. } See BUTYRIC ETHERS (p. 695).

Butyrate of Barium. $C^4H^7BaO^2 + 2aq.$—Obtained by neutralising butyric acid with baryta-water. The filtered solution evaporated in the cold yields long flattened prisms, which are quite transparent, and contain 2 at. water. They melt at a temperature below 100° C., without any loss of weight, to a transparent liquid. The salt dissolves in 2·27 pts. of water at 10°, and rotates on the surface. When butyrate of barium is crystallised from a hot concentrated solution, it contains 10·5 per cent. of water = 1 at. water of crystallisation, its formula being $C^4H^7BaO^2 + aq.$

Butyrate of Copper. $C^4H^7CuO^2 + H^2O$.—According to Chevreul, and to Pelouze and Gélis, this salt contains 2 at. water; according to Liès-Bodart, 1 at. water. It is obtained by the addition of a cupric salt to a solution of butyrate of potassium. The bluish-green precipitate formed is crystallised from boiling water, which yields it in crystals of the monoclinic or oblique prismatic system. By prolonged ebullition with water, the salt is partially decomposed into subsalt and free butyric acid. By distillation at about 250° C., butyrate of copper is completely decomposed into a liquid which appears to be pure butyric acid, a gas composed of equal volumes of carbonic oxide and carburetted hydrogen, and a residue of finely divided metallic copper mixed with carbon. When butyrate of copper is rapidly heated to a high temperature, there is produced, along with other substances, a white crystalline body, which is cuprous butyrate. A compound corresponding to Schweinfurt-green (p 15) is obtained by mixing a solution of butyrate of copper with solution of arsenious acid. A yellowish-green amorphous precipitate forms, which afterwards becomes crystalline, and exhibits the pure green colour belonging to Schweinfurt-green. It is a double salt of arsenite and butyrate of copper, $C^4H^7CuO^2.2AsCuO^2$.

Butyrate of Calcium. $C^4H^7CaO^2$ (at 140°C.).—Obtained like the barium-salt. Crystallises in delicate needles; melts on being heated in its water of crystallisation, which it gives off with tolerable facility. The dry salt, on being distilled, gives an oily distillate, consisting principally of butyral and butyrone. This salt rotates when thrown on water. It dissolves in 5·7 pts. of water at 15° but crystallises out so completely when the solution is heated, that the whole becomes solid. On cooling, it again becomes liquid.

Butyrate of Calcium and Barium.—The aqueous solution of 2 pts. butyrate of calcium, and 3 pts. butyrate of barium, deposits octahedrons of this double salt on spontaneous evaporation.

Butyrate of Iron.—Iron does not decompose dilute butyric acid, but gradually oxidises at the expense of a portion of the acid, the oxide combining with the remainder. A yellowish basic salt which separates, appears to be soluble in a large quantity of water.

Butyrate of Ethyl. See BUTYRIC ETHERS (p. 695).

Butyrates of Lead.—The *neutral* salt, $C^4H^7PbO^2$, is obtained in fine silky needles by abandoning the solution of lead-oxide in butyric acid to spontaneous evaporation over oil of vitriol. The same salt is precipitated by butyric acid from a solution of neutral acetate of lead, as a colourless very heavy oil, which solidifies after some time only. *Basic-salt*, $C^4H^7PbO^2.Pb^2O$. Alkaline butyrates give a copious white precipitate with solutions of subacetate of lead. When a mixture of acetic and butyric acids is saturated with lead-oxide, rose coloured crystals of basic butyrate of lead are formed. These are decomposed by the carbonic acid of the air, but are held in solution by the acetate which adheres to them.

Butyrate of Magnesium. $2(C^4H^7MgO^2) + 5aq.$—Beautiful white laminæ, like crystallised boric acid. The water of crystallisation is easily expelled.

Mercurous Butyrate.—White shining scales, like mercurous acetate.

Butyrate of Methyl. See BUTYRIC ETHERS (p. 696).

Butyrate of Potassium. $C^4H^7KO^2$.—Carbonate of potassium is neutralised with aqueous butyric acid, and the solution evaporated. Crystallises in indistinct cauliflower-like groups. Very deliquescent; dissolves in 0·8 of water at 15° C. Rotates on water. There appears to be an *acid* butyrate of potassium. When butyrate of potassium is distilled with an equal quantity of arsenious anhydride, there is obtained, besides secondary products, an oily liquid blackened by reduced arsenic, and smelling like alkarsin; it is either alkarsin or the term corresponding to it in the butyric series (p. 412.)

Butyrate of Sodium is like the potassium-salt, but less deliquescent.

Butyrate of Silver. $C^4H^7AgO^2$.—Butyrate of potassium mixed with nitrate of silver forms white shining scales, like acetate of silver. The salt does not deflagrate when heated, but leaves metallic silver mixed with a little charcoal.

Butyrate of Strontium. $C^4H^7SrO^2$ (dry).—Long flat needles like the barium-salt; fusible; soluble in 3 pts. of water.

Butyrate of Zinc. $C^4H^7ZnO^2$.—Aqueous butyric acid dissolves carbonate of zinc at ordinary temperatures; the filtered solution evaporated in vacuo leaves shining fusible laminæ. The aqueous solution is decomposed by repeated evaporation into basic salt and free butyric acid.

Substitution-derivatives of Butyric Acid.

DIBROMOBUTYRIC ACID. $C^4H^6Br^2O^2$.—Cahours (Ann. Ch. Phys. [3] xix. 495) obtained an acid of this composition, by the action of bromine on citraconate or itaconate of potassium, to which he gave the name *bromotriconic acid.* It is now commonly regarded as a brominated derivative of butyric acid, and as such finds its description here. When bromine is gradually added, until slightly in excess, to a solution of citraconate of potassium in 1½ pts. of water, carbonic acid is evolved, and a heavy yellowish oil is deposited, which is a mixture of two substances, the one an acid, the other a neutral oil. This is washed with water and treated with potash, which dissolves out the acid, and leaves the neutral oil unchanged. On adding dilute acid to the alkaline solution, the acid is deposited sometimes as a heavy yellowish oil, sometimes in fine crystalline needles: the two substances are identical in composition.

The oily acid has a slight amber colour; it has a peculiar odour, feeble at ordinary, but irritating at higher temperatures. It is much heavier than water, in which it is slightly soluble; it is quite soluble in alcohol and in ether. It is partially decomposed by distillation, with formation of hydrobromic acid fumes, and leaves a carbonaceous residue. Sometimes the oily acid changes spontaneously into a mass of crystals. It is attacked by nitric acid with disengagement of red fumes. Strong potash-ley dissolves it, disengaging a peculiar odour, after which the addition of acid no longer precipitates an oil.

The oily acid forms with *ammonia* an acid salt, $C^4H^5(NH^4)Br^2O^2.C^4H^6Br^2O^2$, which crystallises in yellowish white unctuous scales, easily soluble in water and in alcohol. The silver-salt, $C^4H^5AgBr^2O^2$, is obtained by adding nitrate of silver to a solution of the ammonia-salt, as a curdy precipitate, which, after standing some time, unites into a pitchy mass.

Dibromobutyric Ether.—$C^4H^5(C^2H^5)Br^2O^2$, is obtained with difficulty. A solution of the acid in absolute alcohol is saturated at 70°—80°C. with hydrobromic acid gas; the solution is distilled; the distillate is mixed with water, and the resulting precipitate is washed first with dilute carbonate of soda, then with pure water, and finally dried over oil of vitriol. It emits an irritating odour when heated, and has a sharp taste.

Further experiments are required to prove that Cahours' bromotriconic acid is the true dibromobutyric acid, and it is to be regretted that its discoverer should not have fully cleared up this point. Cahours obtained the following results in attempting to obtain dibromobutyric acid directly. Bromine was added to a solution of butyrate of potassium, until a few drops of a brominated acid were precipitated; the whole was then evaporated to dryness, dissolved in alcohol, filtered, and a few drops of sulphuric acid added, which precipitated an acid different from butyric acid and less odorous, but soluble in water and in alcohol. It did not appear to be identical with bromotriconic acid.

DICHLOROBUTYRIC ACID. $C^4H^6Cl^2O^2$. (Pelouze and Gélis, Ann. Ch. Phys. [3] x. 447.)—The best method of preparing this acid is to pass dry chlorine gas in bright sunshine, through about 40 grm. of butyric acid, placed in a Liebig's bulb-apparatus. At first, the absorption is very rapid; subsequently, hydrochloric acid is disengaged, and the liquid assumes a yellowish-green colour. The absorption becomes slower and more difficult, and the current of chlorine must be continued for several days before it ceases to be absorbed. Dry carbonic acid gas is now passed through it, at a temperature of 80°—100° C. to expel the hydrochloric acid: the residue is dichlorobutyric acid.

It is a colourless viscid liquid, heavier than water, and having a peculiar odour, somewhat like that of butyric acid. It is insoluble in water, but entirely soluble in alcohol. It can be distilled to a great extent without alteration, but a portion always decomposes. It burns with a green-edged flame.

Its potassium-, ammonium-, and sodium-salts are soluble. Its silver-salt is sparingly soluble.

Dichlorobutyric Ether, $C^4H^5(C^2H^5)Cl^2O^2$, is prepared by gently heating an alcoholic solution of dichlorobutyric acid with sulphuric acid. An oily compound ether having an ethereal odour, is deposited, which is washed with water and distilled.

TETRACHLOROBUTYRIC ACID. $C^4H^4Cl^4O^2$. (Pelouze and Gélis, *loc. cit.*)—This acid is produced by the continued action of chlorine upon butyric acid in bright sunshine: the chlorobutyric acid at first formed is ultimately converted into a white, solid, crystalline mass, which when pressed between paper, and crystallised from ether, is obtained in the form of white oblique, rhombic prisms, which melt at 140° C., distil without decomposition, and smell like butyric acid. Its silver-salt, $C^4H^3AgCl^4O^2$, is sparingly soluble.

Tetrachlorobutyric Ether. $C^4H^3(C^2H^5)Cl^4O^2$.—In a solution of tetrachlorobutyric acid in several times its bulk of alcohol, the addition of oil of vitriol immediately produces a crystalline mass, which melts at a gentle heat, and separates into two layers, the heavier of which is tetrachlorobutyric ether. It has an ethereal odour, and burns with a green flame, giving off white fumes of hydrochloric acid.

THIOBUTYRIC ACID, $C^4H^8OS = \left.\begin{matrix}C^4H^7O\\ H\end{matrix}\right\}S$. *Sulphobutyric acid.* (Ulrich, Ann. Ch. Pharm. cix. 280.)—This acid is produced by the action of pentasulphide of phosphorus on butyric acid (p. 691). The substances in equivalent quantities are distilled together in a flask furnished with an inverted condensing apparatus, the action, which is violent at first, being assisted towards the end by gentle heating. After it has continued for several hours, the mixture is distilled, and the reddish liquid, which contains butyric acid and dissolved sulphur, as well as thiobutyric acid, is subjected to fractional distillation, the thiobutyric acid passing over at 130° C. It is a colourless liquid, of almost insupportable and persistent odour; boils at 130° C.; is sparingly soluble in water, readily in alcohol, and dissolves sulphur with yellowish colour. With *acetate of lead*, it forms a bulky white precipitate of thiosulphate of lead, C^4H^7PbOS, soluble in a large quantity of hot water, also in hot alcohol, and separating on cooling, in small colourless crystals. The salt decomposes readily, with separation of sulphide of lead.

E. A.

BUTYRIC ANHYDRIDE. *Anhydrous Butyric Acid.* $C^8H^{14}O^3 = \left.\begin{matrix}C^4H^7O\\ C^4H^7O\end{matrix}\right\}O$. (Gerhardt, Ann. Ch. Pharm. lxviii. 127.)—The formation of this body is analogous to that of the organic anhydrides in general, that is to say, it is formed by the action of chloride of butyryl on an alkaline butyrate.

It is prepared by treating 4 pts. of dry butyrate of sodium with **2** pts. of oxychloride of phosphorus, the oxychloride being added drop by drop to the butyrate, as in the preparation of acetic anhydride. The reaction consists of two stages, the first being the formation of chloride of butyryl and phosphate of sodium:

$$3C^4H^7NaO^2 + POCl^3 = Na^3PO^4 + 3C^4H^7OCl,$$

and the second, the formation of butyric anhydride by the action of this chloride on another portion of butyrate of sodium. When the reaction is complete, the mass is distilled, and the distillate redistilled over butyrate of sodium, in order to convert any remaining chloride of butyryl. The distillate from this is finally rectified, those parts only being collected which boil at 190° C.; the portions which pass over below this point contain butyric acid, the formation of which cannot well be avoided, from the deliquescent nature of the butyrate of sodium.

Like acetic anhydride (p. 20), butyric anhydride may be prepared by the action of benzoic chloride on butyrate of sodium. Five pts. of benzoic chloride are mixed with 8 pts. of butyrate of sodium in a retort, and distilled, and the distillate rectified, at first over butyrate of sodium, and then alone.

Butyric anhydride is a colourless, very mobile, and highly refracting liquid, of specific gravity 0·978 at 12·5° C. Its odour is very strong, but not disagreeable, and rather resembling butyric ether than butyric acid. It boils at 190°, and its vapour-density has been found to be 5·38. Exposed to the air, it gradually attracts moisture, and is converted into butyric acid. Poured into water, it does not dissolve like butyric acid, but rises to the surface as a colourless oil. In contact with aniline, it becomes heated, and forms butyranilide (phenylbutyramide):

$$(C^4H^7O)^2O + 2(N.H^2.C^6H^5) = 2(N.H.C^6H^5.C^4H^7O) + H^2O.$$

E. A.

BUTYRIC ETHERS. These compounds are formed from butyric acid by the substitution of 1 at. of an organic radicle, such as ethyl, methyl, &c. for 1 at. of hydrogen. They are for the most part formed by the direct action of butyric acid on the alcohols.

Butyrate of Allyl. $C^7H^{12}O^2 = C^4H^7(C^3H^5)O^2$.—Obtained by distilling butyrate of silver with iodide of allyl. After rectification, it is a colourless oily liquid, lighter than water, soluble in ether, smelling like butyrate of ethyl, and boiling at about 140° C. Heated with potash, it yields allyl-alcohol and butyrate of potassium. (**Cahours** and **Hofmann**, Phil. Trans. 1857, p. 555.)

Butyrate of Amyl. $C^9H^{18}O^2 = C^4H^7(C^5H^{11})O^2$, is a liquid boiling at 17·6° C. (**Delffs**). Specific gravity 0·852 at 15°. Index of refraction = 1·402.

Butyrate of Ethyl. *Butyric Ether.* $C^6H^{12}O^2 = C^4H^7(C{\cdot}H^5)O^2$.—This ether is readily produced by the action of butyric acid on alcohol, sulphuric acid being likewise present. It is also formed, according to Berthelot, by distilling a mixture of 1 pt. common ether, 3 pts. butyric acid, and 7 to 8 pts. sulphuric acid; but the distillate contains a large quantity of free butyric acid. To prepare it, 2 pts. butyric acid are dissolved in an equal weight of strong alcohol, and 1 pt. sulphuric acid is added to the mixture. The liquid becomes heated, and butyric ether immediately rises to the surface; but to complete the transformation, it is necessary to heat the mixture for a short time to about 80° C. The butyric ether is then decanted, shaken up several times with water, finally with addition of chalk and chloride of calcium, then dried over chloride of calcium and distilled.

Butyrate of ethyl is a transparent, colourless, very thin liquid, of specific gravity 0·90193. Boils at 119° C., under a pressure of 0·7465 mm. Vapour-density = 4·04. It has an agreeable odour, like that of pine-apples, and a sweetish taste, with bitter after-taste. It is very sparingly soluble in water, but dissolves in all proportions in alcohol and in ether. It is slowly decomposed by potash, into butyrate of potassium and alcohol.

To the presence of small quantities of butyric ether, the peculiar flavour of pine-apples, melons, and some other fruits, is due. Its formation in the fruit receives an obvious explanation, from the readiness with which the saccharine matters present pass on the one hand, into lactic and butyric acids, and on the other, into alcohol. The pine-flavoured rum, known as pine-apple rum, owes its flavour to the presence of this ether. When freshly distilled from molasses, rum has but little flavour, but this comes out on keeping, owing to the fact that a small quantity of butyric acid contained in it, gradually combines with the alcohol to form ether.

A solution of butyric ether is very extensively used in perfumery, and in confectionery, under the name of pine-apple oil. It is prepared for this purpose by the following process. Butter is saponified by a strong solution of potash-ley; the soap is dissolved in very little absolute alcohol, and to the solution is added a mixture of alcohol and sulphuric acid, until a strongly acid reaction is set up. The whole is then distilled, heat being applied as long as anything comes over with a fruity odour.

Butyrate of Ethylene, $C^{10}H^{18}O^4 = \left.\begin{array}{r}(C^4H^7O)^2\\(C^2H^4)''\end{array}\right\} O^2$, is obtained by heating bromide of ethylene for several days to 100° C. with butyrate of silver and a little free butyric acid, exhausting the product with ether, and distilling fractionally:

$$2(C^4H^7O.Ag.O) + C^2H^4Br^2 = 2AgBr + (C^4H^7O)^2.(C^2H^4)''.O^2.$$

It is a colourless liquid, of specific gravity 1·024 at 0° C.; smells like butyric acid, and boils at 239° to 241° C. (A. Wurtz, Ann. Ch. Phys. [3] lv. 400.)

Butyrate of Glyceryl. See **Butyrins.**

Butyrate of Methyl. $C^5H^{10}O^2 = C^4H^7(CH^3)O^2$.—A mixture of 2 pts. butyric acid with 1 pt. of wood-spirit and 1 pt. of strong sulphuric acid, becomes heated and separates into two layers, the upper of which is butyrate of methyl. In order that the transformation may be complete, it is well to agitate the mixture, and even to maintain it for some time at a temperature of from 50°—80° C. The product is purified like the ethyl-compound.

Butyrate of methyl is a transparent colourless liquid of specific gravity 1·0293. Boils at 102° C. Specific heat is 0·4918. Latent heat of vapour, 87·33. Vapour-density, 3·52. It has a pleasant odour, somewhat resembling that of pine-apples. It is scarcely soluble in water, but perfectly soluble in alcohol and in ether. E. A.

BUTYRIDIN. This name was given by Berthelot to a compound formed from butyric acid and glycerin, to which he at first assigned the formula $C^{14}H^{26}O^7$ ($= 2C^4H^8O^2 + 2C^3H^8O^3 - 3H^2O$), but which he afterwards found to be identical with dibutyrin (p. 695).

BUTYRINS. (Berthelot, Ann. Ch. Phys. [3] xli. 261.)—By the direct action of butyric acid on glycerin, a series of compounds analogous to the acetins is obtained. They are *monobutyrin*, $C^7H^{14}O^4$, *dibutyrin*, $C^{11}H^{20}O^5$, and *tributyrin*, $C^{15}H^{26}O^6$. They contain the elements of glycerin and butyric acid, minus those of water. Their formation may be thus expressed:

$$\begin{array}{cccccccc}
\underset{\text{Glycerin.}}{C^3H^8O^3} & + & \underset{\substack{\text{Butyric}\\\text{acid.}}}{C^4H^8O^2} & - & H^2O & = & \underset{\substack{\text{Mono-}\\\text{butyrin.}}}{C^7H^{14}O^4} \\
\underset{\text{Glycerin.}}{C^3H^8O^3} & + & \underset{\substack{\text{Butyric}\\\text{acid.}}}{2(C^4H^8O^2)} & - & 2H^2O & = & \underset{\text{Dibutyrin.}}{C^{11}H^{20}O^5} \\
\underset{\text{Glycerin.}}{C^3H^8C^3} & = & \underset{\substack{\text{Butyric}\\\text{acid.}}}{3(C^4H^8O^2)} & - & 3H^2O & = & \underset{\text{Tributyrin.}}{C^{15}H^{26}O^6}
\end{array}$$

Viewing glycerin as a triatomic alcohol, we may consider the butyrins as glycerin $\left.\begin{array}{r}C^3H^5{}'''\\H^3\end{array}\right\} O^3$, in which 1, 2, or 3 at. of hydrogen are replaced by the radicle butyryl, C^4H^7O.

The butyrins are decomposed by alkalis, and also by the alkaline earths, baryta and lime, with formation of a butyrate and elimination of glycerin. Dissolved in alcohol and treated with hydrochloric acid, they yield butyric ether and glycerin.

Monobutyrin, $C^7H^{14}O^4 = \left.\begin{array}{r}(C^3H^5)'''\\H^2\\C^4H^7O\end{array}\right\} O^3$.—This body is formed, but only in small proportions, by exposing a mixture of butyric acid with excess of glycerin, to the action of the sun or of diffused daylight for several months. It is also obtained by heating butyric acid with glycerin to a temperature of 200° C. for three hours, care being taken not to exceed this temperature. It is a colourless, neutral, odoriferous, oily liquid, having an aromatic and bitter taste, without any after-taste. At −40° C., it remains liquid, and as mobile as at ordinary temperatures. It rapidly acidifies when exposed to the air.

Dibutyrin, $C^{11}H^{20}O^5 = \left.\begin{array}{r}(C^3H^5)'''\\H\\(C^4H^7O)^2\end{array}\right\} O^3$.—Whenever in the preparation of monobutyrin, the temperature exceeds 220° C., some dibutyrin appears to be formed, but it is best prepared by heating a mixture of glycerin and butyric acid to 275° for several hours. It is a colourless, neutral, oily, odoriferous liquid, of specific gravity 1·081. It volatilises at 320° without perceptible alteration. Cooled down to −40°, it remains liquid, but its fluidity diminishes. By aqueous ammonia, it is decomposed, with formation of butyramide.

Tributyrin, $C^{15}H^{26}O^{6} = \left.\begin{matrix}(C^{3}H^{5})'''\\(C^{4}H^{7}O)^{3}\end{matrix}\right\}O^{3}$. — This substance is formed by heating butyrin with 10 to 15 times its weight of butyric acid to 240° C. for four hours. It is a neutral, oily liquid, with an odour analogous to that of the preceding compounds, and a pungent taste, with irritating aftertaste. It is very soluble in alcohol and ether, but insoluble in water.

Natural Butyrin. — A butyrin which is probably tributyrin, is contained in small quantities in butter, along with caproin, caprin, olein, and margarin. It has not been obtained free from these substances. According to Pelouze and Gélis, this compound may be prepared artificially by gently heating a mixture of butyric acid, glycerin, and concentrated sulphuric acid. On adding a large quantity of water, a slightly yellowish oil separates, which must be washed with water, in which it is insoluble. It is soluble in all proportions in alcohol and ether, from which solutions it is separated by the addition of water. Saponified by potash, it yields glycerin and butyrate of potassium. It has not been obtained pure, and is most probably a mixture of the butyrins above described.
E. A.

BUTYRITE. A compound formed from butyric acid and mannite in the same manner as the butyrins are formed from butyric acid and glycerin. Its properties have not been described. (Berthelot, Compt. rend. xxxviii. 688.)

The same name is sometimes applied to bog-butter (*q. v.*)

BUTYROCHLORHYDRIN. By the action of hydrochloric acid on a mixture of butyric acid and glycerin, a product (first observed by Pelouze) is obtained, which, according to Berthelot (Ann. Ch. Phys. [3] xli. 303), is a mixture of the compounds $C^{3}H^{6}(C^{4}H^{7}O)ClO^{2}$ and $C^{3}H^{5}(C^{4}H^{7}O)Cl^{2}O$, that is to say, of chlorhydrin ($C^{3}H^{7}ClO^{2}$) and dichlorhydrin ($C^{3}H^{6}Cl^{2}O$), in each of which 1 at. H is replaced by butyryl. No method of separating these two compounds has yet been devised.

BUTYROLEIC ACID. Bromeis (Ann. Ch. Pharm. xlii. 63) stated that butter contains an oily acid resembling oleic acid in most respects, but differing from it in not yielding sebacic acid by dry distillation. Bromeis assigned to this acid the formula $C^{34}H^{30}O^{4}.HO$. It appears, however, from the experiments of Gottlieb, that it is really identical with oleic acid, and exhibits the characters observed by Bromeis only after it has been considerably altered by exposure to the air.

BUTYROLIMNODIC ACID. See Bog-butter (p. 617).

BUTYROLACTIC ACID. $C^{7}H^{12}O^{4} = \left.\begin{matrix}(C^{3}H^{4}O)''\\C^{4}H^{7}O\\H\end{matrix}\right\}O^{2}$. — This acid, which is derived from lactic acid, $(C^{3}H^{4}O)''.H^{2}.O^{2}$, by the substitution of 1 at. butyryl for 1 at. hydrogen, has not yet been obtained in the free state; but Wurtz (Compt. rend. xlviii. 1092) has obtained its *ethyl-salt*, $(C^{3}H^{4}O)''.C^{4}H^{7}O.C^{2}H^{5}.O^{2}$, by digesting chlorolactate of ethyl with an alcoholic solution of butyrate of potassium in the water-bath for several days, then filtering to separate chloride of potassium, treating the filtrate with chloride of calcium, and rectifying:

$$\underset{\text{Chlorolactate of ethyl.}}{(C^{3}H^{4}O)''.C^{2}H^{5}.Cl.O} + \underset{\text{Butyrate of potassium.}}{C^{4}H^{7}O.K.O} = KCl + \underset{\text{Butyrolactate of ethyl.}}{(C^{3}H^{4}O)''.C^{4}H^{7}O.C^{2}H^{5}.O^{2}}.$$

It is an oily liquid, of specific gravity 1·024 at 0° C., having an odour something like that of butyric acid, insoluble in water, soluble in alcohol, and boiling between 200° and 210° C. The formation and constitution of this compound tend strongly to support the opinion that lactic acid is dibasic. (See Lactic Acid.)

BUTYRONE. $C^{7}H^{14}O$.—This body is the acetone or ketone of the butyric series, and is, therefore, homologous with acetic acetone. It represents butyral, in which 1 at. of hydrogen in the radicle is replaced by trityl:

$$\underset{\text{Butyral.}}{\left.\begin{matrix}C^{4}H^{7}O\\H\end{matrix}\right\}} \qquad \underset{\text{Butyrone.}}{\left.\begin{matrix}C^{4}H^{6}(C^{3}H^{7})O\\H\end{matrix}\right\}}$$

Its formation is analogous to that of its homologue, acetone. Butyrate of calcium carefully distilled in small portions is decomposed into butyrone and carbonate of calcium:

$$\underset{\text{Butyrate of calcium.}}{2(C^{4}H^{7}CaO^{2})} = \underset{\text{Carbonate of calcium.}}{Ca^{2}CO^{3}} + \underset{\text{Butyrone.}}{C^{7}H^{14}O}.$$

But when larger quantities are decomposed, the results are not so precise. The crude product is composed of at least four substances, butyral, butyrone, and two other substances of the ketone series. The butyrone is obtained pure by rectification, those parts being collected which boil at 140°—145° C. and these are again rectified, until a product of constant boiling point is obtained.

Butyrone, when pure, is a colourless limpid liquid, having a peculiar penetrating odour, and density = 0·83. It boils at 144° C., and its vapour-density has been found to be 4·0, which corresponds to two volumes for the formula $C^7H^{14}O$. Surrounded by a mixture of solid carbonic acid and ether, it solidifies to a crystalline mass. It is insoluble in water, but quite soluble in alcohol. It burns with a luminous flame. It immediately takes fire in contact with chromic acid. It is energetically attacked by nitric acid, with formation of nitropropionic acid, $C^3H^4(NO^2)O^2$, and of an ethereal liquid, which is probably butyrate of trityl, $C^4H^7(C^3H^7)O^2$.

Distilled with pentachloride of phosphorus, butyrone yields a compound, $C^7H^{13}Cl$, which Chancel terms *chlorobutyrone.* It is a colourless liquid, of penetrating odour, lighter than water, and insoluble therein. It boils at 116° C. Its alcoholic solution does not cloud nitrate of silver.

From the crude product of the distillation of butyrate of calcium, two substances with definite boiling points may be separated by treating the crude distillate with acid sulphate of sodium, to remove butyral and butyrone, and subjecting the remaining liquid to fractional distillation. One of these boils at 180° C., and has the specific gravity 0·827. It has the formula $C^8H^{16}O$, which is that of methyl-butyrone, $C^7H^{13}(CH^3)O$, or methyl-œnanthyl, $CH^3.C^7H^{13}O$. The latter view of its composition is suggested by the fact that it yields œnanthic acid when oxidised by nitric acid. The other compound boils at 222° C., and is a pale yellow liquid, which becomes solid at 12° C. Its composition is $C^{11}H^{22}O$, which would correspond to tetryl-butyrone, $C^7H^{13}(C^4H^9)O$, or tetryl-œnanthyl, $C^4H^9.C^7H^{13}O$. It appears to yield butyric and œnanthic acids by oxidation. (Limpricht, Ann. Ch. Pharm. cviii. 183.)

According to Friedel (Ann. Ch. Pharm. cviii. 125), the crude liquid obtained by the distillation of butyrate of calcium, contains, amongst other products, ethyl-butyryl, $C^6H^{12}O = C^2H^5.C^4H^7O$, a colourless liquid having a biting taste, an aromatic odour like that of butyrone, specific gravity = 0·833 at 0° C., and vapour-density = 3·58, and a much smaller quantity of methyl-butyryl, $C^5H^{10}O = CH^3.C^4H^7O$, of specific gravity 3·827 at 0° C., and vapour-density 3·13. E. A.

BUTYRONITRIC ACID. This name has been applied to the product of the action of nitric acid on butyrone.

BUTYRONITRILE or **CYANIDE OF TRITYL.** $C^4H^7N = C^3H^7.CN$.—This body is best prepared by distilling butyrate of ammonium or butyramide with anhydrous phosphoric acid:

$$\underset{\text{Butyrate of ammonium.}}{C^4H^{11}NO^2} - 2H^2O = \underset{\text{Butyronitrile.}}{C^4H^7N.}$$

It is a transparent colourless oil, of specific gravity 0·795 at 12·6° C., and boiling at 118·5°. It has an agreeable aromatic odour resembling that of bitter-almond oil. It dissolves in boiling potash, with evolution of ammonia and formation of butyrate of potassium:

$$\underset{\text{Butyronitrile.}}{C^4H^7N} + KHO + H^2O = \underset{\text{Butyrate of potassium.}}{C^4H^7KO^2} + NH^3.$$

E. A.

BUTYRUM ANTIMONII. A name applied to trichloride of antimony, on account of its buttery consistence and fusibility. Other chlorides of like consistence have also received similar names, *e. g. Butyrum stanni, Butyrum zinci,* &c.

BUTYRUREID. Syn. of BUTYRYL-UREA.

BUTYRYL. C^4H^7O.—The radicle of butyric acid and its derivatives. The following compounds of it are known:

Bromide of butyryl	$C^4H^7O.Br$
Chloride of butyryl	$C^4H^7O.Cl$
Iodide of butyryl.	$C^4H^7O.I$
Hydride of butyryl (butyric aldehyde)	$C^4H^7O.H$
Oxide of butyryl (butyric anhydride)	$(C^4H^7O)^2.O$
Hydrate of butyryl (butyric acid)	$C^4H^7O.H.O$
Butyryl-propyl (butyrone)	$C^4H^7O.C^3H^7$
Butyryl-urea or butyral-urea	$N^2(CO)''.H^3.C^4H^7O.$

The name butyryl has likewise been applied to the hydrocarbon C^4H^7, sometimes regarded as the radicle of butyric acid.

BROMIDE OF BUTYRYL, $C^4H^7O.Br$, is produced by the action of bromide of phosphorus on butyric acid at 90°—100° C., purified by washing with water and rectification. (Béchamp.)

CHLORIDE OF BUTYRYL. $C^4H^7O.Cl$.—This body, like its homologue, chloride of acetyl, is produced by the action of 1 at. oxychloride of phosphorus on 3 at. butyrate of sodium:

$$\underset{\text{Butyrate of sodium.}}{3C^4H^7NaO^2} + \underset{\text{Oxychloride of phosphate.}}{POCl^3} = \underset{\text{Chloride of butyryl.}}{3C^4H^7OCl} + \underset{\text{Phosphate of sodium.}}{Na^3PO^4}.$$

The powdered butyrate is gradually added to the oxychloride contained in a retort: for if the oxychloride were at once poured on the butyrate, a large quantity of anhydrous butyric acid would be formed. The mixture is distilled, and the liquid distillate rectified over a small quantity of butyrate of sodium, the temperature being kept as low as possible, in order to prevent the anhydrous acid formed during the rectification from distilling over with the chloride.

Chloride of butyryl is a colourless, mobile, strongly refracting liquid, heavier than water, and fuming slightly in the air. Its boiling point is 95°. It has a pungent odour like both butyric and hydrochloric acids. It is immediately decomposed by water into hydrochloric and butyric acids:

$$\underset{\text{Chloride of butyryl.}}{C^4H^7OCl} + H^2O = \underset{\text{Butyric acid.}}{C^4H^8O^2} + HCl.$$

With butyrate of sodium it yields chloride of sodium and butyric anhydride:

$$C^4H^7OCl + C^4H^7NaO = NaCl + C^8H^{14}O^3.$$

With ammonia it yields butyramide and hydrochloric acid:

$$C^4H^7OCl + NH^3 = C^4H^7O.H^2.N + HCl.$$

Iodide of Butyryl, $C^4H^7O.I$, produced by distilling butyrate of potassium with iodide of phosphorus, is a brownish liquid, which melts in contact with the air, and boils between 146° and 148° C. (Cahours.) E. A.

BUTYRYL-UREA. See Carbamide.

BUXINE. An alkaloid said to exist in all parts of the box-tree (*Buxus sempervirens.*) According to Fauré (J. Pharm. xvi. 428) it is obtained as an uncrystallisable mass, by boiling the aqueous solution of the alcoholic extract of the bark with magnesia, exhausting the resulting precipitate with alcohol, decolorising with animal charcoal, and evaporating. According to Couerbe (J. Pharm. January 1854, p. 51), it may be obtained in the crystalline form by treating the sulphate with nitric acid, whereby an admixed resin is destroyed or rendered insoluble, and precipitating by an alkali.

Buxine has a bitter taste and excites sneezing; it blues reddened litmus-paper; is nearly insoluble in cold water; dissolves readily in alcohol, sparingly in ether; insoluble in alkalis. It is decomposed by nitric acid. Its salts are more bitter than the base itself, and yield a gelatinous precipitate with alkalis. The sulphate is said to form crystalline nodules.

Trommsdorff (Tromm. N. J. xxv. [2] 66) obtained from box-leaves a substance probably identical with Fauré's buxine.

BYSSOLITE. A name applied to the fine capillary implanted crystals of actinolite, found on the St. Gothard and in the Tyrol.

BYSSUS MYTILI. The bundle of threads by which the common muscle (*Mytilus edulis*) adheres to other bodies, consists, according to Scharling (Ann. Ch. Pharm. xli. 48), of a mass resembling horny tissue, containing a small quantity of fat. According to Lavine (J. Chem. méd. xii. 124) it contains the salts which occur in sea-water.

BYTOWNITE. A granular massive mineral occurring in large boulders near Bytown, Canada West. The grains have one perfect cleavage and indications of another oblique thereto. Hardness = 6 to 6·5. Specific gravity 2·80 (Thomson); 2·733 (Hunt). It has a greenish-white colour and vitreous lustre, pearly on the cleavage surface. Translucent. According to Thomson (J. pr. Chem. viii. 489) it contains 47·57 per cent. silica, 29·65 alumina, 9·06 lime, 7·6 soda, 3·57 ferrous oxide, 0·2 magnesia, whence it appears to be a variety of barsowite (p. 517), the alumina being partly replaced by ferric oxide and the lime by soda. T. S. Hunt (Sill. Am. J. [2] xii. 213) regards it as a variety of anorthite. A dark bluish-green granular mineral or rock from Perth, Canada, which has been called Bytownite, is considered by the same chemist as a mixture of bytownite and hornblende.

C

CABBAGE. (See BRASSICA.)—Infusion of red cabbage, obtained by pouring hot water on the leaves, is a convenient test for acids and alkalis. A certain quantity of alkali, just sufficient to neutralise the acid in the juice, turns it blue; any further quantity changes the blue to green; and acids turn it red.

CABBAGIINE. A bitter principle, obtained from the cabbage-tree (*Geoffraga inermis*, or *G. jamaicensis*), also called *Jamaicine* (*q. v.*)

CABOCLE. A mineral resembling red jasper or felsite, found in the diamantiferous sand of the province of Bahia. It has a density of 3·14 to 3·19; scratches glass slightly; turns white before the blowpipe, but does not melt; dissolves partially in warm strong sulphuric acid, leaving a white earthy residue, which dissolves in the acid at a higher temperature, and is precipitated therefrom by water. Damour (L'Institut. xxi. 78) found in the red massive mineral, phosphoric acid, alumina, lime, baryta, ferrous oxide, and water.

CACAO. The seeds or leaves of the *Theobroma cacao* and other species of the same genus (Nat. Ord. *Sterculiaceæ*), natives of South America and the West Indies, which are extensively cultivated in those countries, and in the tropical parts of Asia and Africa, are remarkable for their nutritive properties, and yield the well-known substances, cocoa and chocolate. They contain large quantities of fatty matter and vegetable albumin, and about 2 per cent. of an organic base, *theobromine*, $C^7H^8N^4O^2$, resembling caffeine. The ash is very rich in phosphoric acid. Shelled beans of good quality exhibit, before roasting, the following composition per cent.: 52 cacao-butter, 20 albumin, fibrin, &c., 2 theobromine, 10 starch, 2 cellulose, 4 inorganic matter, and 10 water, besides small quantities of colouring matter and essential oil. (Payen, Traité de Pelouze et Frémy, vi. 529.)

Cacao-beans have also been analysed by Tuchen (Inaugural Dissertation, Göttingen, 1857; and by A. Mitscherlich (*Der Cacao und die Chocolade*, Berlin, 1859), with the following results:

	Tuchen.						Mitscherlich.	
	Guaya-quil.	Suri-nam.	Caracas.	Para.	Marag-nan.	Trinidad.	Guaya-quil.	Caracas.
Theobromine	0·63	0·56	0·55	0·66	0·38	0·48	1·2—1·5	
Cacao-red	4·56	6·61	6·18	6·18	6·56	6·22	3·5— 5	
Cacao-butter	36·38	36·97	35·08	34·48	38·25	36·42	45—49	46—49
Glutin	2·96	3·20	3·21	2·99	3·13	3·15	13—18	
Starch	0·53	0·55	0·62	0·28	0·72	0·51	14—18	13·5—17
Gum	1·58	0·69	1·19	0·78	0·63	0·61		
Extractive matter	3·44	4·18	6·22	6·62	3·32	5·48		
Humic acid	8·57	7·25	9·28	8·63	8·03	9·25		
Cellulose	30·50	30·00	28·66	30·21	29·77	29·86	5·8	
Ash	3·03	3·00	2·91	3·00	2·92	2·98	3·5	
Water	6·20	6·01	5·58	5·55	5·48	4·88	5·6—6·3	
Starch-sugar	—	—	—	—	—	—	0·34	
Cane-sugar	—	—	—	—	—	—	0·26	
	98·38	99·02	99·48	99·38	99·19	99·84		

Mitscherlich's results do not differ from those of Payen, more than might be expected in the analysis of different varieties; those of Tuchen, which differ widely from both the preceding, probably refer to the unshelled beans.

The starch of cacao-beans exhibits granules of peculiar form, quite distinct from those of the cereals and leguminosæ; by this means, the flour of either of the latter may be detected when used to adulterate chocolate.

The ash of the shelled beans has been analysed by Letellier (Pelouze et Frémy, *loc. cit.*), and by Zedeler (Ann. Ch. Pharm. lxxviii. 348), with the following results:

K^2O	Na^2O	Ca^2O	Mg^2O	SO^3	CO^2	P^2O^5	$3Fe^4O^3.P^2O^5$	Cl	SiO^2	
33·4		11·0	17·0	4·5	1·0	29·6		0·2	3·3	(Letellier).
37·14	1·23	2·9	16·0	1·5	1·2	39·6	0·17	1·7		(Zedeler).

The kernels of the theobroma are used as an article of nutriment, either in the natural state, or prepared in various ways. The simplest and best form is that of the seeds roughly crushed, termed *cocoa-nibs*, which, however, require two hours' boiling, as, owing to the peculiar nature of the inner seed-coating, which passes down into the substance of the cotyledons, the prolonged application of heat and moisture is necessary to dissolve the contents. *Flake-cocoa* is merely the seeds crushed between rollers. To prepare *chocolate*, the beans, after being carefully picked, to free them from mouldy or worm-eaten ones, are gently roasted over a fire in an iron cylinder, with holes in the ends to allow the vapour to escape. When the aroma begins to be well developed, the process is considered complete. The beans are then turned out, cooled, and freed from their husks by fanning and sifting. The husks, which often amount to 20 or 25 per cent. of the beans, should not be thrown away, as they contain half their weight of soluble or mucilaginous matter, which yields a tolerable nutriment. The seeds are then converted into a paste, either by trituration in a mortar heated to 130° F., or more generally by a machine impelled by steam, and the paste is put into moulds and sent into the market; it always improves by keeping. Sometimes the beans, before being roasted, are left to rot or ferment in heaps, in order to separate the kernels from the soft pulpy mass which surrounds them in the fruit.

The chocolate of different countries varies according to its mode of preparation, and the ingredients contained in it. When the kernels alone are used, or only a little sugar is added, the chocolate is called "Chocolat de santé." But vanilla, cloves, cinnamon, and other aromatics, are frequently added; also rice, almonds, starch, &c. Simple chocolate is mostly preferred in this country, the perfumed sorts in France, Italy, and Spain, where the consumption is immense. (See *Ure's Dictionary of Arts, Manufactures, and Mines*, i.; also *Penny Cyclopædia*, art. THEOBROMA.)

Cacao-butter, or *Cacao-fat*, is extracted from the beans by pounding them in a slightly heated mortar, till they are reduced to a pulp, then adding a small quantity of water, and squeezing the pulp in a cloth between two plates of metal previously heated to the temperature of boiling water. It has an agreeable taste and odour, is white, semi-transparent, insoluble in water, soluble, especially with aid of heat, in alcohol, ether, and oil of turpentine. It has the consistence of suet, melts at 30° C., but does not resume the solid state till cooled to 23°. It consists chiefly of stearin, with a little olein. It is used more in France than in this country, for making soap, candles, and pommade. The soap made from it must not be confounded with that made from *cocoa-nut oil*, which is a very different product, obtained from the cocoa palm (*Cocos nucifera*).

Cacao-red is the colouring matter of cacao-beans. It is separated by precipitating the aqueous or alcoholic decoction of the beans with acetate of lead, and decomposing the washed precipitate with sulphuretted hydrogen. The solution thus obtained is neutral, has a bitter taste, and yields lilac or greyish precipitates with acetate of lead and protochloride of tin; dark green, or brown-green, with ferric salts; and green of various shades, or sometimes violet with ferrous salts; the colour of the precipitate varies in each case, according as the cacao-red in the solution is more or less mixed with other substances.

The solution of cacao-red absorbs oxygen during evaporation, and becomes acid, the colouring matter being in fact converted into a kind of tannic acid. This modified cacao-red gives, for the most part, green precipitates with iron and lead salts; that obtained from Guayaquil cacao, gives pale reddish precipitates with acetate of lead and with lime-water, reddish-white with sulphate of magnesium and ammonium. It is precipitated by gelatin, whereas unaltered cacao-red is not.

The alteration produced by the roasting of cacao-beans, appears to affect the cacao-red more than any of the other constituents.

CACHALAGUA, or **CANCHA LAGUA**, is the South American name of the *Chironia chilensis*, a gentianaceous plant, which, according to Bley (Arch. Pharm. xxxvii. 85), contains resin and a bitter principle.

CACHOLONG. A variety of OPAL (*q. v.*)

CACHOUTANNIC, or **CACHUTIC ACID.** See CATECHU.

CACODYL. See ARSENIDES OF METHYL (p. 403).

CACOTHELINE. $C^{20}H^{22}N^4O^9 = C^{20}H^{22}(NO^2)^2N^2O^5$.—A product of the decomposition of brucine by nitric acid (p. 682). It partly separates in orange-yellow crystalline flakes after the action has ceased, and an additional quantity may be obtained by precipitating the red liquor with alcohol. From a solution in water strongly acidulated with nitric acid, it separates in yellow scales. It is but very sparingly soluble in boiling water, still less in boiling alcohol, and insoluble in ether. When heated, it decomposes suddenly, in the manner characteristic of nitro-compounds. Exposed to diffused light in a stoppered bottle, it soon becomes dark brown on the surface. Potash dissolves it easily, forming a yellowish-brown liquid. Ammonia dissolves it immediately, forming a yellow liquid, which on boiling changes first to green, afterwards to brown. Cacotheline unites with metallic oxides: with baryta, it forms a soluble compound, containing $2C^{20}H^{22}N^4O^9.Ba^2O$. It combines also with acids, but the salts are decomposed by water. When *dichloride of platinum* is added to a solution of cacotheline in hydrochloric acid, the liquid, after a few hours, yields a crystalline precipitate containing 48 per cent. platinum = $C^{20}H^{22}N^4O^9.HCl.PtCl^2$.

When cacotheline is left for some hours in the red nitric solution in which it has been formed, it changes into another body, which has the colour of chrome-yellow, is insoluble in water, and explodes when heated. (Strecker, Compt. rend. xxxix. 62.)

CACOXENE. A native ferric phosphate, found in the Hrbeck mine, near Zbiron in Bohemia, in radiated tufts of yellow or brownish-yellow colour, becoming brown on exposure. Specific gravity = 3·38. Hardness = 3—4. Of the following analyses, *a* and *b* are by von Hauer (Jahrb. geolog. Reichsanst. 1854, 67); *c* by Richardson (Thomson's Mineralogy, i. 476):

	P^2O^5	Fe^4O^3	H^2O	Ca^2O	Mg^2O	SiO^2	
a . .	19·63	47·64	32·73	—	—	—	= 100
b . .	25·74	41·46	32·83	—	—	—	= 100
c . .	20·5	43·1	30·2	1·1	0·9	2·1	= 97·9

a and *c* agree nearly with the formula $2Fe^4O^3.P^2O^5 + 12$ aq., or $3fe^2O.2fe^3PO^4 + 12$ aq. The analysis *b*, which, however, is said by von Hauer to have been made with less pure material, approaches more nearly to $3Fe^4O^3.2P^2O^5 + 20$ aq. Former analyses by Steinmann, which showed 10—11 per cent. alumina, were doubtless made with impure specimens. (Rammelsberg's Mineralchemie, p. 331.)

CACTUS. Vogel obtained from the flowers of *Cactus speciosus*, by extraction with weak alcohol, 30 per cent. of a carmine-red dye, insoluble in ether and in absolute alcohol. The petals, after the removal of this substance, yielded to a mixture of alcohol and ether, from 5 to 10 per cent. of a scarlet substance. Both these colouring matters are soluble in water. (J. Pharm. xxii. 664.)

F. Field (Chem. Soc. Qu. J. iii. 57) has analysed the ash of a species of cactus (not named) growing in Chili. The fresh plant yielded 1·35, the dry plant 16·79 per cent. of ash, containing in 100 pts. 57·15 pts. of soluble and 42·73 of insoluble salts. The air-dried plant yielded 85·09 per cent. water. The composition of the ash per cent. is: 7·83 K^2O, 28·19 Na^2O, 10·65 Ca^2O, 7·75 Mg^2O, 0·34 Mn^4O^3, 6·09 SO^3, 16·49 SiO^2, 6·40 P^2O^5, 1·38 phosphates of calcium, magnesium, and iron, and 14·87 NaCl.

CADET'S FUMING LIQUID. See ARSENIDES OF METHYL (p. 403).

CADIE-GUM. A very pure kind of gamboge, probably from *Hebradendron cambogioïdes*.

CADMIUM. *Symbol* Cd. *Atomic weight* 56. Atomic volume in the gaseous state = 1.

This metal is frequently found associated with zinc, and derives its name from *cadmia fossilis*, a denomination by which the common ore of zinc was formerly known. It appears to have been discovered about the same time (1818) by Stromeyer (Gilb. Ann. lx. 193) and by Hermann (*ibid.* lix. 95, 113; lxvi. 274), but its more exact investigation is due to Stromeyer.

Cadmium occurs in small quantity in several varieties of native sulphide, carbonate, and silicate of zinc, viz. in the radiated blende of Przibram in Hungary, to the amount of 2 or 3 per cent.; in the blende of Nuissière, to the amount of 1·14 per cent.; in silicate of zinc from Freiberg and from Derbyshire; in carbonate of zinc from Mendip; in carbonate and silicate of zinc from the Cumberland mines; in the zinc ores of the Harz and of Silesia. The zinc flowers obtained as a secondary product in the smelting of the Silesian ores, contain, according to Hermann, as much as 11 per cent. of cadmium. Commercial English zinc frequently also contains cadmium. The only pure native compound of cadmium is the sulphide called *Greenockite*, found at Bishopstown in Renfrewshire.

Preparation.—In the process of reducing ores of zinc, the cadmium which they contain comes over among the first products of distillation, owing to its greater volatility. It may be separated from zinc in an acid solution by sulphydric acid, which throws down the cadmium as a yellow sulphide. This sulphide dissolves in concentrated hydrochloric acid, affording the chloride of cadmium, from which the carbonate may be precipitated by an excess of carbonate of ammonia. Carbonate of cadmium is converted by ignition into the oxide; and the latter yields the metal when mixed with one-tenth of its weight of pounded coal, and distilled in a glass or porcelain retort, at a low red heat.

Properties.—Cadmium is a white metal, with a slight tinge of blue. It has a strong lustre, and takes a fine polish; by exposure to the air, it gradually acquires a whitish-grey tarnish. It has a compact texture and fibrous fracture, and easily crystallises in regular octahedrons. It is soft, though harder and more tenacious than tin; very flexible, and crackles like tin when bent; very malleable and ductile. Its specific gravity is, after fusion, 8·604, after hammering, 8·6944. Specific heat 0·05669 (Regnault), 0·0576 (Dulong and Petit). Cadmium melts below a red heat, and volatilises somewhat below the boiling point of mercury without emitting any particular odour. The density of its vapour as determined by experiment at 1040° C. is 3·94, referred to air as unity (Deville and Troost, Ann. Ch. Pharm. cxiii. 46). Now the calculated value for a condensation to 1 vol. is found by multiplying the atomic weight by the density of hydrogen $= 56 \times 0{\cdot}0693 = 3{\cdot}88$. Hence cadmium-vapour follows the usual law of condensation (p. 441).

Cadmium dissolves in hot hydrochloric or dilute sulphuric acid, taking the place of the hydrogen in the acid; but its best solvent is nitric acid. The bromide, iodide, and many of the organic salts of cadmium, the acetate for example, are soluble in water; the rest, *e. g.* the carbonate, borate, phosphate, and arsenate, are insoluble in water, and are obtained by precipitation. Most cadmium-salts are colourless; they have a disagreeable metallic taste and act as emetics. The solutions, even of the neutral salts, redden litmus. Those cadmium-salts which are insoluble in water are soluble in sulphuric, hydrochloric, or nitric acid, also in ammoniacal salts.

Cadmium, in nearly all its compounds with electro-negative elements, plays the part of a monatomic radicle, the chloride being $CdCl$, the oxide Cd^2O, &c.

CADMIUM, ALLOYS OF. But few alloys of cadmium are known. 100 pts. *copper* retain at a red heat 82·2 pts. cadmium, forming an alloy having nearly the composition $CdCu^2$. It is very brittle, has a fine-grained scaly structure, and a yellowish white colour. With *mercury*, cadmium forms a hard, brittle, silver-white amalgam, which crystallises in octahedrons, and contains 21·7 per cent. cadmium $= CdHg^2$. 100 pts. *platinum* retain at a red heat, 117·3 pts. cadmium $= Cd^2Pt$. The alloy is almost silver-white, very brittle, very fine-grained, and refractory in the fire. (Stromeyer.)

CADMIUM, BROMIDE OF. $CdBr$.—Cadmium absorbs bromine-vapour at a heat near redness, forming white fumes of the bromide, which crystallises on cooling, and when strongly heated sublimes in white nacreous laminæ. The *hydrated bromide*, $2CdBr.H^2O$, obtained by dissolving the oxide or carbonate in hydrobromic acid, forms white efflorescent needles, which give off half their water at 100° C., and the rest, without melting, at 200°.

Bromide of cadmium forms crystalline compounds with the bromides of potassium, sodium, and barium. The *barium-salt*, $CdBr.BaBr + 2aq.$, forms large, shining, colourless crystals, isomorphous with the corresponding chloride. A solution of the bromides of cadmium and *potassium* in equivalent proportions, first yields crystals containing $2CdBr.KBr + \frac{1}{2}aq.$, afterwards crystals of $CdBr.KBr$; both compounds resemble the corresponding double chlorides (C. v. Hauer, J. pr. Chem. lxiv. 477; lxvii. 169). A solution of equivalent quantities of bromide of cadmium and bromide of *sodium* yields the compound $2CdBr.NaBr + \frac{5}{2}aq.$ in small, shining, six-sided tables. (Croft, Chem. Gaz. 1856, p. 121.)

CADMIUM, CHLORIDE OF. $CdCl$.—A solution of oxide of cadmium in hydrochloric acid yields a crystalline hydrated chloride, $CdCl.H^2O$; and this when fused yields the anhydrous chloride in the form of a transparent, laminated, pearly mass, which melts at a heat below redness, and sublimes at a higher temperature in transparent micaceous laminæ.

A solution of chloride of cadmium mixed with excess of ammonia yields, by spontaneous evaporation, *ammoniochloride of cadmium*, $NH^3.CdCl$, or *chloride of cadmammonium*, $NH^3Cd.Cl$.—A *triammonio-chloride of cadmium*, $3NH^3.CdCl$, is obtained by exposing dry pulverised chloride of cadmium to the action of gaseous ammonia. It gives off ⅔ of its ammonia when exposed to the air, and is converted into the preceding compound. (Croft, Phil. Mag. [3] xxi. 355.)

Chloride of cadmium forms crystalline compounds with the chlorides of many other metals. These compounds, which have been particularly studied by C. v. Hauer (J. pr. Chem. lxiv. 477; lxvii. 169; Jahresber. d. Chem. 1855, p. 392; 1856, p. 394; Chem. Soc. Qu. J. viii. 250), crystallise by evaporation from mixed solutions of the component chlorides. The following have been obtained:

The *ammonium-salt*, $NH^4Cl.CdCl + \frac{1}{2}aq.$, crystallises in slender needles; the mother-liquor yields by spontaneous evaporation, transparent shining rhombohedrons of $2NH^4Cl.CdCl$.

Potassium-salts. $KCl.2CdCl + \frac{1}{2}aq.$ separates, by spontaneous or by more rapid evaporation, from a solution of 1—2 at. chloride of potassium to 1 at. chloride of cadmium, in fine silky needles, which give off their water at 100° C., and at a higher temperature melt and give off part of their chlorine. The mother-liquor, or a solution of at least 3 at. chloride of potassium to 1 at. chloride of cadmium, yields by spontaneous evaporation, the salt 2KCl.CdCl, in large limpid crystals, somewhat less (?) soluble than the preceding.

Sodium-salt. NaCl.CdCl + $\frac{3}{2}$aq. (air-dried.)—Small, turbid, watery crystals, which give off 1 at. water at 100 C., and the remainder at 150°—160°.

Barium-salt. BaCl.CdCl + 2 aq.—Separates from a solution of equivalent quantities of the two chlorides, in large shining crystals, which are permanent in the air, lose half their water at 100° C., the rest at 160°, and at a red heat give off part of their chlorine, and melt to a colourless liquid, which does not crystallise. According to Rammelsberg's determination, the crystals are monoclinic, the obliquely inclined axes making an angle of 75° 45′. Ratio of the clinodiagonal, orthodiagonal, and principal axis = 0·8405 : 1 : 0·5128. Observed faces, $\infty P . \infty P \infty . (\infty P \infty) . + P . - P . 0P . (2P \infty)$. Inclination of faces, $\infty P : \infty P \infty = 140° 50′$; $\infty P : 0P = 101° 0′$; $0P : + P = 137° 40′$.

Strontium-salt. SrCl.2CdCl + $\frac{7}{2}$aq.—Crystallises from a solution of 1 to 2 at. chloride of cadmium and 1 at. chloride of strontium in transparent, colourless, acuminated crystals.

Calcium-salts.—A solution of 3 at. chloride of calcium to 4 at. chloride of cadmium deposits the salt CaCl.2CdCl + $\frac{7}{2}$aq. in deliquescent bevelled prisms, arranged in stellate groups. A hot concentrated solution of 2 at. chloride of cadmium and 1 at. chloride of calcium deposits, on cooling, large deliquescent crystals of the salt 2CaCl. CdCl + aq.

Magnesium-salts.—A solution of 1 to 2 at. chloride of cadmium to 1 at. chloride of magnesium yields MgCl.2CdCl + 6 aq. in large transparent crystals. From a solution of 2 at. chloride of magnesium to 1 at. chloride of cadmium, the salt 2MgCl.CdCl + 12 aq. separates in deliquescent tabular crystals.

Manganese-salt. MnCl.5CdCl + 6 aq.—Crystallises from a solution of 2 at. chloride of cadmium and 1 at. chloride of manganese, in pale rose-red or colourless prisms.

Iron-salt. FeCl.2CdCl + 6 aq.—Crystallises from a solution of equivalent quantities of the two chlorides, in colourless prisms, which soon turn green and yellow by exposure to the air.

Cobalt-salt. CoCl.2CdCl + 6 aq.—Somewhat deliquescent prisms, of the colour of chloride of cobalt.

Nickel-salts. NiCl.2CdCl + 6 aq. crystallises by spontaneous evaporation from a solution containing the two salts in the required proportions, in dark green prisms; and the mother-liquor, or the original solution, if it contains a slight excess of chloride of nickel, yields 2NiCl.CdCl + 6 aq. in large, dark green, rhombic prisms.

Copper-salt. CuCl.CdCl + 2 aq.—Crystallises from a solution containing equivalent quantities, in slender shining prisms, grouped in tufts, green when moist, blue when dry.

Chloride of cadmium forms double salts with the hydrochlorates of many organic bases. Greville Williams (Chem. Gaz. 1855, 450) obtained the *quinoline-salt*, $C^9H^7N.HCl.2CdCl$, as a hard crystalline mass; and other compounds have been obtained by J. Galletly (Ed. N. Phil. J. iv. 94), viz.:

Cinchonine-salt.	$C^{20}H^{24}N^2O.HCl.CdCl + \frac{1}{2}$ aq.
Morphine-salts.	$C^{17}H^{19}NO^3.HCl.7CdCl + 2$ aq., and $C^{17}H^{19}NO^3.HCl.2CdCl + \frac{3}{2}$ aq.
Narcotine-salt.	Semi-crystalline, sparingly soluble mass.
Nicotine-salt.	$C^{10}H^{14}N^2.2HCl.5CdCl$. Crystallisable.
Lutidine-salt.	$C^7H^9N.HCl.3CdCl$. Very soluble feathery crystals.
Piperine-salt.	$C^{34}H^{38}N^2O^6.2HCl.9CdCl + 3$ aq. Straw-yellow needles.
Strychnine-salt.	$C^{21}H^{22}N^2O^2.HCl.CdCl$. Sparingly soluble in water.
Toluidine-salt.	$2(C^7H^9N.HCl).3CdCl +$ aq. Very soluble scales.

CADMIUM, DETECTION AND ESTIMATION OF. 1. *Blowpipe Reactions.*—All cadmium-compounds, when heated on charcoal in the inner blowpipe flame with carbonate of sodium or cyanide of potassium, give a brown incrustation of cadmic oxide. A little cadmium, in presence of zinc, may be detected by heating the mixture with carbonate of sodium for an instant in the inner flame, when a slight incrustation of cadmic oxide will be formed. Much longer heating is required for the formation of zinc-oxide. With *borax* and *microcosmic salt*, cadmic oxide forms a bead which is yellowish while hot, colourless when cool.

2. *Liquid Reactions.*—*Zinc* immersed in a solution of a cadmic salt, throws down metallic cadmium in dendrites. *Sulphydric acid gas*, passed through cadmium-solutions, even when a large excess of acid is present, precipitates the whole of the cadmium in the form of sulphide, which has a lemon-yellow colour at first, but afterwards becomes orange-yellow. A similar effect is produced by *alkaline sulphydrates*, the precipitate being insoluble in excess. The hydrated sulphides of manganese, iron, cobalt, and nickel, when recently precipitated, likewise throw down sulphide of cad-

mium from cadmic salts (Anthon, J. pr. Chem. x. 353). *Caustic alkalis* throw down white hydrate of cadmium, very easily soluble in a slight excess of ammonia, but insoluble in potash or soda. Sulphydric acid likewise precipitates sulphide of cadmium from the solution in excess of ammonia. The *neutral* and *acid carbonates* of *ammonium, potassium*, and *sodium* throw down white carbonate of cadmium, insoluble in excess of the alkaline carbonates. If the salt contains a large quantity of free acid, the precipitate dissolves in excess of carbonate of ammonia, but not otherwise (Stromeyer). *Phosphate of sodium* throws down white phosphate of cadmium. *Oxalic acid* and *alkaline oxalates* precipitate white oxalate of cadmium, insoluble in alkaline oxalates, but easily soluble in ammonia. The white precipitate produced by *ferrocyanide of potassium*, and the yellow precipitate produced by the *ferricyanide*, are soluble in hydrochloric acid. The addition of hyposulphite of sodium and hydrochloric acid does not produce a precipitate of sulphide of cadmium; neither is any precipitate produced by chromic acid, succinic acid, alkaline benzoates, or tincture of galls.

Cadmium is the only metal which forms a yellow sulphide insoluble in sulphide of ammonium.

3. *Quantitative Estimation.*—Cadmium is best precipitated from its solutions by carbonate of sodium; it is thereby obtained as a carbonate, which, by ignition, yields the brown oxide containing 87·5 per cent. of the metal.

4. *Separation from other Elements.*—From the metals of the second and fourth groups, and from all non-metallic elements except selenium and tellurium, cadmium may be separated by sulphuretted hydrogen; from *selenium, tellurium*, and the metals of Group 1, Subdivision A (p. 217), by the insolubility of its sulphide in sulphide of ammonium. The sulphide is then dissolved by nitric acid, and the cadmium precipitated by carbonate of sodium, as above.

From *bismuth, lead*, and *mercury*, cadmium may be separated by the solubility of its oxide in ammonia, or of its cyanide in cyanide of potassium: from *lead* also by sulphuric acid, and from *mercury* by precipitating the latter in the metallic state by protochloride of tin. From *palladium*, it is also separated by the solubility of its cyanide in cyanide of potassium; from *silver*, by precipitating that metal as chloride. From *copper*, cadmium is separated by carbonate of ammonium, an excess of which redissolves the copper and not the cadmium: or better, by treating the solution of the two metals with excess of cyanide of potassium, which precipitates and redissolves them both, and passing sulphuretted hydrogen through the liquid, whereby the cadmium is precipitated, while the copper remains dissolved. (See COPPER.)

5. *Atomic Weight of Cadmium.*—Stromeyer found that 114·352 pts. protoxide of cadmium, Cd^2O, yielded 14·352 O; whence $14·352 : 100 = 16 : Cd^2$; and $Cd = \frac{1600}{2 \times 14·352} = 55·7$. Dumas (Ann. Ch. Pharm. cxiii. 27), from the mean of six experiments on the quantity of nitrate of silver required to precipitate the chlorine from chloride of cadmium, found for the atomic weight of cadmium, numbers varying from 55·89 to 56·38. He regards 56 as very near to the true value.

CADMIUM, FLUORIDE OF, CdF, is deposited from the aqueous solution on evaporation, in white, indistinctly crystalline crusts. It dissolves sparingly in pure water, more readily in aqueous hydrofluoric acid. (Berzelius.)

CADMIUM, IODIDE OF. CdI.—Prepared either in the dry way, or by digesting cadmium with iodine and water. Crystallises in large, transparent, six-sided tables, which are not altered by exposure to the air. It melts easily, and solidifies again in the crystalline form; gives off iodine at a higher temperature. Dissolves readily in water and alcohol, and crystallises unchanged from the solutions. Sulphydric acid slowly precipitates sulphide of cadmium from the aqueous solution.

Two *ammonio-iodides of cadmium* are known, viz. $NH^3.CdI$, which is deposited in small crystals from a solution of iodide of cadmium in hot aqueous ammonia; and $3NH^3.CdI$, which is a white powder produced by gently heating iodide of cadmium in ammonia-gas. (Rammelsberg, Pogg. Ann. xlviii. 153.)

Iodide of Cadmium and Potassium, CdI.KI + aq. crystallises in confused octahedrons from a solution of the two iodides in equivalent proportions. In like manner are obtained: $NH^4I.CdI$ + aq., apparently isomorphous with the potassium-salt; NaI.CdI + 3aq. in deliquescent prisms; BaI.CdI + ½ aq., also deliquescent; and SrI.CdI + 4aq. in large crystals, which deliquesce in moist, and effloresce in dry air. (Croft, Chem. Gaz. 1856, p. 121.)

CADMIUM, NITRIDE OF. (?) When an electric current is passed through a solution of sal-ammoniac, the positive pole being formed of cadmium, and the negative pole of platinum, the latter becomes covered with a spongy, lead-grey mass, which, after washing and drying, has a density of 4·8; 5 grains of it gave off when heated, 0·18 to 0·25 cub. in. of nitrogen gas free from hydrogen, and left a yellowish-green residue, containing globules of cadmium. (Grove, Phil. Mag. [3] xix. 99.)

CADMIUM, OXIDES OF. Cadmium forms two oxides, viz. a protoxide, Cd^2O, and a suboxide, Cd^4O. The protoxide dissolves in acids without evolution or absorption of oxygen, and forms salts of corresponding composition: *e. g.* the sulphate, Cd^2SO^4, the nitrate $CdNO^3$, &c. These are indeed the only salts of cadmium; the suboxide when treated with acids, yields metallic cadmium and a protosalt.

Suboxide of Cadmium, Cd^4O, is obtained by heating the oxalate to about the melting point of lead. It is a green powder, resembling oxide of chromium, and is resolved by heat or by acids, into metallic cadmium and the protoxide. It does not however yield metallic cadmium when treated with mercury: hence it appears to be a definite compound, and not a mere mixture of the metal with the protoxide.

Protoxide of Cadmium, or *Cadmic Oxide*, Cd^2O, or CdO.—Cadmium, heated in the air, takes fire and is converted into protoxide. The same compound is formed when vapour of cadmium and aqueous vapour are passed together through a red-hot tube; but it is most easily prepared by igniting the hydrate, carbonate, or nitrate. It varies in colour from brown-yellow to blackish, according to the mode of preparation. By boiling cadmium for some time in a long-necked flask, the oxide may be obtained in purple crystals. Its specific gravity is 6·9502. It is quite fixed in the fire, and does not melt at the strongest white heat. It is easily reduced by charcoal before the blowpipe, and emits vapours of metallic cadmium, which is immediately reoxidised, and forms a red or brown deposit on the charcoal (p. 703). It is insoluble in water, but unites with it, forming a hydrate.

Hydrate of Cadmium, CdHO, is precipitated by potash from *dilute* solutions of cadmic salts; it may be obtained in indistinctly crystalline warty groups, by the action of aqueous ammonia on metallic cadmium in contact with iron or copper. It is white, absorbs carbonic acid from the air, is insoluble in the fixed alkalis, dissolves readily in caustic ammonia, but not in carbonate of ammonia. It dissolves easily in sulphuric, nitric, hydrochloric, and acetic acid.

CADMIUM, PHOSPHIDE OF. Grey, with faint metallic lustre; very brittle; difficult to fuse. Burns in the air with a bright flame, producing cadmic phosphate. Hydrochloric acid dissolves it, with evolution of phosphoretted hydrogen.

CADMIUM, SULPHIDE OF. Cd^2S, or CdS.—This compound occurs in the form of *Greenockite*, and is prepared as a pigment known by the name of *jaune brillant*. It is formed with difficulty by fusing cadmium with sulphur,—more readily by igniting cadmic oxide with sulphur; precipitated in yellow flakes when sulphydric acid or an alkaline sulphydrate is brought in contact with a cadmium-salt. The native sulphide crystallises in double six-sided pyramids and other forms of the hexagonal system, with cleavage parallel to the terminal and lateral edges of a six-sided prism. Specific gravity 4·8 (Brooke), 4·908 (Breithaupt). Hardness equal to that of calcspar. Of diamond lustre, semi-transparent, honey-yellow; yields an orange-yellow or a brick-red powder; becomes carmine-red when heated. Decrepitates when heated somewhat strongly (Brooke, Breithaupt). The artificial sulphide, in the precipitated state, is an orange-yellow powder, which, when heated to redness, becomes first brownish and then carmine-red. It melts at an incipient white heat, and solidifies on cooling, in transparent, lemon-yellow, micaceous laminæ. It is not volatile at any temperature (Stromeyer). Specific gravity of the fused artificial sulphide, 4·605. (Karsten).

In dilute hydrochloric acid it dissolves with difficulty, even when the acid is heated; but if the acid be strong, the sulphide dissolves with ease, even at ordinary temperatures, with violent evolution of sulphuretted hydrogen, and without separation of sulphur. At a red heat it slightly decomposes vapour of water; at a white heat, oxide of cadmium is formed (Regnault). It dissolves in nitric acid, with evolution of sulphuretted hydrogen and separation of sulphur. Very soluble in ammonia.

CADMIUM-ETHYL. Cadmium appears to form with ethyl a compound analogous to zinc-ethyl; but it has not yet been obtained in the pure state. Wanklyn (Chem. Soc. Qu. J. ix. 193), by heating cadmium-foil with half its weight of iodide of ethyl dissolved in an equal volume of ether in a sealed tube, obtained a liquid which passed over in fractional distillation between 180° and 220° C., gave off first white and then brown vapours on exposure to the air, and at length took fire, emitting a brown smoke. It smelt like zinc-ethyl, and was decomposed by water, with effervescence and formation of a white precipitate. It contained 36·8 per cent. cadmium, whereas the formula C^2H^5Cd requires 66 per cent. Hence the distillate appears to have contained about 56 per cent. of cadmium-ethyl, the remainder consisting of ether, iodide of ethyl, and perhaps certain hydrocarbons. (See also Sonnenschein, J. pr. Chem. lxvii. 169.)

CÆSIUM. *Symbol* Cs. *Atomic weight* = 124.—An alkali-metal, the chloride of which has lately been discovered by Bunsen and Kirchhoff, in the mother-liquors of certain saline-waters in Germany. Its compounds give a spectrum distinguished by two blue lines, one rather faint at about the middle of the blue space of the normal spectrum, and the other much brighter, situated more towards the violet end. It was by this peculiar spectrum that the metal was discovered (page 214).*

CAFFEIC ACID. See Caffetannic Acid.

CAFFEINE or **THEINE.** $C^8H^{10}N^4O^2$, or $C^{16}H^{10}N^4O^4$. (Gm. xiii. 223; Gerh. i. 542.)—Caffeine was discovered in coffee by Runge, in the year 1820 (Materialien zur Phytologie, 1821, i. 146). Oudry (Mag. Pharm. xix. 49), in 1827, found in tea a crystalline subtance, which he called theine, supposing it to be a distinct compound; but Jobst (Ann. Ch. Pharm. xxv. 63) and Mulder (Pogg. Ann. xliii. 160), in 1838, showed that it was identical with caffeine. Martius, in 1840 (Ann. Ch. Pharm. xxxvi. 93), discovered the same substance in guarana, the dried pulp of *Paulinia sorbilis*; and Stenhouse, in 1843 (Phil. Mag. [3] xxiii. 426), obtained it from Paraguay tea, the leaves and twigs of *Ilex Paraguayensis*. The same chemist has shown (Phil. Mag. [4] vii. 21) that it exists in the leaves as well as in the berries of the coffee-plant. The exact composition of caffeine was first demonstrated in 1832 by Pfaff and Liebig (Ann. Ch. Pharm. i. 17). Its combinations and reactions have been especially studied by Stenhouse (*loc. cit.;* also Ann. Ch. Pharm. xlv. 366; xlvi. 227), Nicholson (Chem. Soc. Qu. J. iii. 321), Péligot (Ann. Ch. Phys. [3] xi. 128) and Rochleder (Ann. Ch. Pharm. lxxi. 1; lxxiii. 56 and 123). Its alkaline nature was first demonstrated by Herzog. (Ann. Ch. Pharm. xxvi. 344; xxix. 171.)

Preparation. a. From Tea or Coffee.—1. The mode of extraction generally adopted is to treat tea or coffee with boiling water and mix the infusion with subacetate of lead to precipitate the tannin. Péligot adds subacetate of lead in excess, then ammonia. The mixture is boiled for some time, the lead-precipitate carefully washed on a filter with boiling water, the filtrate freed from excess of lead by sulphuretted hydrogen, and after a second filtration, evaporated at a gentle heat. On cooling, it yields an abundant crystallisation of nearly pure caffeine, and an additional quantity may be obtained by concentrating the mother-liquor and leaving it to crystallise.—2. Caffeine may also be obtained by saturating the free acid contained in infusion of tea or coffee with carbonate of potassium; treating the liquor with with infusion of gall-nuts; mixing the precipitate with dry hydrate of lime; exhausting the mixture with alcohol; expelling the alcohol from the filtrate by distillation; and dissolving the residue in boiling water or boiling ether (Robiquet and Boutron, J. Pharm. xxiii. 108).—3. Five pts. of ground coffee are mixed with 2 pts. of slaked lime, and the mixture is exhausted with alcohol in a displacement apparatus. The extract is then dried, pulverised, and again treated with alcohol; the alcohol separated from the extracts by distillation; the fat oil which floats on the surface is removed; the watery liquid is evaporated to the crystallising point; and the crystals of caffeine are pressed and decolorised by animal charcoal: 50 kilogrammes of coffee thus treated yielded more than 250 grammes of caffeine (Versmann, Arch. Pharm. [2] lxviii. 148).—4. Ground coffee is digested for a week with commercial benzene, which takes up caffeine and oil of coffee. Both remain behind when the benzene is distilled off, and may be separated by hot water, which dissolves the caffeine and leaves it in large crystals when evaporated. The oil may also be dissolved out by ether, which leaves the caffeine undissolved (Vogel, Chem. Centralb. 1858, p. 367).—5. Payen exhausts coffee with ether, then washes it thoroughly with alcohol of 60 per cent., concentrates the solutions to a slightly syrupy consistence, and mixes them with three times their volume of 85 per cent. alcohol, whereupon the liquid separates into two layers, the lower being viscid and the upper fluid. The latter, which contains the greater part of the caffeine, is decanted, and freed from the greater part of the alcohol by distillation; and the syrupy residue is mixed with one-fourth of its bulk of alcohol at 90° C., and left to itself in a cool place: it then deposits crystals, which are recrystallised from alcohol. They consist, according to Payen, of caffetannate (chlorogenate), of caffeine and potassium, and when submitted to dry distillation, yield a sublimate of caffeine (Ann. Ch. Phys. [3] xxvi. 108).—6. Caffeine or theine being volatile, may also be prepared by sublimation. For this purpose, waste useless tea is gradually heated in a sublimation apparatus, like that used for preparing benzoic acid, but not so strongly as to decompose the theine. Part of the sublimate is quite pure; the rest may be purified by recrystallisation from water. (Heiynsius, J. pr. Chem. xlix. 317.)

According to the results of an extensive series of experiments made by Graham, Stenhouse, and Campbell (Chem. Soc. Qu. J. ix. 33), coffee contains from 0·8 to

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* See Appendix to this volume.

1 per cent. of caffeine; tea about 2 per cent. **Stenhouse** (Ann. Ch. Pharm. lxxxix. 246) obtained from a sample of black tea from Kimaon on the Himalaya, 1·97 per cent. theine, and from another sample of good black tea 2·13 per cent. According to **Péligot** (Ann. Ch. Phys. [3] xi. 68), Hyson tea contains from 2·2 to 3·4 per cent., and gunpowder tea from 2·2 to 4·1 per cent. of theine. According to Robiquet and Boutron (*loc. cit.*) Martinique coffee yields 0·36 per cent., Mocha coffee 0·206, and Cayenne coffee 0·2 per cent. of caffeine.

b. From Guarana.—Guarana mixed with $\frac{3}{10}$ of its weight of quick lime is repeatedly boiled with alcohol of 33° Beck; the filtrate is evaporated a little; the greenish fatty oil which separates on cooling is removed; the residual alcoholic liquid completely evaporated; and the dry residue is heated: caffeine then sublimes, at first yellowish-white, afterwards quite white.—2. Twenty-four grammes of guarana powder are boiled with a quart of water; the cold solution is precipitated with basic acetate of lead; the bulky brownish-red precipitate filtered off, and repeatedly digested with hot water; and the lead is separated from the filtrate by sulphuretted hydrogen. The liquid separated from the sulphide of lead is evaporated in the water-bath to dryness; the residue dissolved in a little boiling alcohol, filtered, and allowed to crystallise; and the crystals thus obtained are purified by pressing and recrystallisation. Guarana contains about 5 per cent. of caffeine. (**Stenhouse.**)

c. From Paraguay Tea.—The filtered decoction is precipitated with neutral acetate of lead and the filtrate with basic acetate (or it is boiled with litharge), and the liquid decanted from the precipitate is evaporated to dryness, a tough, dark brown, hygroscopic mass then remaining. From this residue, caffeine may be obtained, either by sublimation, or by reducing it to powder, mixing it with sand, and treating it with ether. After distilling off the ether, feebly coloured caffeine crystallises, and may be purified by repeated crystallisation. The product amounts to 0·13 per cent. of the Paraguay tea. (**Stenhouse.**)

[For a full account of the methods of preparing caffeine, see Gmelin's Handbook, *loc. cit.*]

Properties.—Caffeine crystallises from water in slender needles, having the aspect of white silk, and containing 8·4 per cent. water of crystallisation ($C^8H^{10}N^4O^2 + H^2O$), which is not given off completely at 150° C. (**Mulder**). Specific gravity of the crystals 1·23 at 19° C. (**Pfaff**). It has a slightly bitter taste, and grates between the teeth. Melts at 178°, and sublimes completely at 185° in capillary and feathery needles (**Mulder**). It is sparingly soluble in cold water and alcohol, still less in ether. Boiling water dissolves it more freely, and the solution solidifies in a pulp on cooling. The crystals which separate from ether and alcohol are anhydrous.

Decompositions.—1. Caffeine, when quickly and strongly *heated*, suffers partial decomposition, giving off vapours which have the odour of methylamine.—2. Strong *sulphuric acid* decomposes it after continued heating.—3. When *chlorine* is passed into a thick magma of caffeine and water, the crystals gradually disappear, and a mixture of several substances is obtained, varying in composition according to the duration of the action. With a comparatively small quantity of chlorine, the products are amalic acid, $C^6H^6N^2O^4$, methylamine and chloride of cyanogen, together with chlorocaffeine, $C^8H^9ClN^4O^2$. The formation of the three first-mentioned products is represented by the equation:

$$C^8H^{10}N^4O^2 + 2H^2O + Cl^4 = C^6H^6N^2O^4 + CH^5N + CNCl + 3HCl.$$

The resulting liquid heated in the water-bath gives off hydrochloric acid, and a gas smelling like chloride of cyanogen, and granular crystals of amalic acid separate, succeeded (if too much chlorine has not been passed through the liquid) by chlorocaffeine in light flocks and crusts. If the action of the chlorine be prolonged, the compound $C^5H^6N^2O^3$, called *nitrotheine* by Stenhouse, *cholestrophane* by Rochleder, and *dimethylparabanic acid* [$C^3(CH^3)^2N^2O^3$] by Gerhardt, is produced:

$$\underset{\text{Amalic acid.}}{C^6H^6N^2O^4} + Cl^2 + H^2O = \underset{\text{Nitrotheine.}}{C^5H^6N^2O^3} + CO^2 + 2HCl.$$

4. Caffeine boiled with *hydrochloric acid* and *chlorate of potassium* yields alloxan or a similar body, the aqueous solution of which colours the skin red and imparts to it a peculiar odour. The solution gives with ammonia the colour of murexid, and with alkalis and ferrous salts the colour of indigo.—5. Strong *nitric acid* boiled with caffeine gives off nitrous fumes, and forms a yellow liquid, which assumes the purple colour of murexid on adding a drop of ammonia (this reaction furnishes a test for caffeine). If the ebullition be continued, the liquid becomes colourless, no longer exhibits the purple colour with ammonia, and yields by evaporation crystals of dimethylparabanic acid (nitrotheine), floating in a mother-liquor containing a salt of methylamine.—6. Caffeine boiled with very strong *potash-ley* evolves a considerable quantity of methylamine.—7. With *soda-lime* it gives off ammonia, forms carbonate of sodium,

carbonate of calcium, and a large quantity of cyanide of sodium. This reaction distinguishes caffeine from piperine, morphine, quinine, and cinchonine, which do not form cyanide of sodium when similarly treated. (Rochleder.)

Compounds of Caffeine.—Caffeine is a weak base: it dissolves in acids, forming salts which have an acid reaction, and are for the most part decomposed by evaporation, caffeine free from acid being deposited.

Hydrochlorate of Caffeine, $C^8H^{10}N^4O^2.HCl$, is obtained in crystals by dissolving caffeine in very strong hydrochloric acid, not diluted either with water or with alcohol, and concentrating by gentle evaporation. If either water or alcohol be added, nothing but caffeine crystallises out. The salt forms large, transparent, efflorescent crystals, belonging to the trimetric system, $\infty P \,.\, \bar{P}\infty \,.\, \infty\breve{P}\infty$. Inclination of the faces, $\infty P : \infty\bar{P} = 118° 30' : \bar{P}\infty : \infty\bar{P}\infty = 116° 30'$.

Chloroaurate of caffeine, $C^8H^{10}N^4O^2.HCl.AuCl^3$, crystallises from alcohol in orange-coloured needles (Nicholson). The *chloromercurate*, $C^8H^{10}N^4O^2.2HgCl$, obtained by mixing an alcoholic solution of caffeine with excess of mercuric chloride, forms needles resembling caffeine, soluble in water, hydrochloric acid, alcohol, and oxalic acid, nearly insoluble in ether. The *cyanomercurate*, $C^8H^{10}N^4O^2.2HgCy$, prepared in like manner forms prisms belonging to the dimetric system, sparingly soluble in cold water and alcohol. The *chloroplatinate*, $C^8H^{10}N^4O^2.HCl.PtCl^2$, forms small distinct orange-yellow crystals, sparingly soluble in water, alcohol, and ether. With *chloride of palladium*, hydrochlorate of caffeine forms a beautiful brown precipitate, and the filtered liquid deposits yellow scales of another compound, not unlike iodide of lead.

A solution of caffeine does not precipitate *sulphate of copper*, *protochloride of tin*, *acetate of lead*, or *mercurous sulphate*. Boiled with *sesquichloride of iron*, it forms, on cooling, a brown-red precipitate, perfectly soluble in water, and probably consisting of a double salt similar to the preceding. With *nitrate of silver*, caffeine forms the compound $AgNO^3.C^8H^{10}N^4O^2$, which separates on mixing concentrated solutions of caffeine and nitrate of silver, in white crystalline hemispheres, adhering firmly to the sides of the vessel. It is sparingly soluble in cold, more readily in hot water and alcohol; detonates when heated.

Sulphate of Caffeine is difficult to crystallise, and is easily decomposed by water.

Tannate of Caffeine is obtained as a white precipitate when an aqueous solution of caffeine is added in excess to aqueous tannic acid. It contains 41·9 per cent. caffeine and 58·1 tannic acid (Mulder). An infusion of tea, by its tannin, also precipitates a solution of caffeine.

CAFFEONE. The aromatic principle of coffee. It may be isolated by distilling 5 or 6 lbs. of roasted coffee with water, agitating the aqueous distillate with ether, and afterwards evaporating the ether. It is a brown oil, heavier than water, slightly soluble in boiling water. An almost imponderable quantity of it is sufficient to aromatise more than a quart of water. (Pelouze et Frémy, Traité, iv. 449.)

CAFFETANNIC ACID. *Caffeic Acid. Chlorogenic Acid.* $C^{35}H^{38}O^{17}$? (Pfaff, 1830, Scher. lxi. 487.—Rochleder, Ann. Ch. Pharm. lix. 300; lxiii. 193; lxvi. 35; lxxxii. 196.—Liebich, *ibid.* lxxi. 97.—Stenhouse, *ibid.* lxxxiii. 244.—Payen, Ann. Ch. Phys. [3] xxvi. 108.—Gerh. Traité, iii. 886.)—This acid exists in coffee berries to the amount of 3 to 5 per cent. as a calcium- and magnesium-salt, and, according to Payen, as a double salt of caffeine and potassium. According to Rochleder, it is also found in Paraguay tea. It is prepared by mixing an alcoholic infusion of coffee or Paraguay tea with water to separate the fatty matter; then boiling the liquid, adding acetate of lead, decomposing the precipitate with sulphuretted hydrogen, and evaporating the filtered liquid. It forms a yellowish brittle mass, which may with difficulty be obtained in colourless, mammellated, crystalline groups. It dissolves easily in water, less in alcohol; has an astringent taste, and reddens litmus strongly. Melts when heated, then chars, and gives off the odour of roasted coffee. By dry distillation it yields water and a thick oil, which solidifies on cooling, and consists of oxyphenic acid (Rochleder). Strong sulphuric acid dissolves it with the aid of heat, forming a blood-red liquid. Distilled with peroxide of manganese and sulphuric acid, it yields quinone (Stenhouse). It dissolves with yellow colour in potash and in ammonia. The ammoniacal solution in contact with the air quickly turns green, producing *viridic acid*, $C^{14}H^{14}O^8$ (?) (Rochleder.)

Caffetannic acid colours ferric salts green. It does not precipitate ferrous salts, but, on adding ammonia, a nearly black precipitate is obtained. It does not precipitate tartar-emetic or gelatin, but precipitates quinine and cinchonine. It reduces nitrate of silver in specular form if the liquid is heated.

The formula of caffetannic acid is not definitely fixed. Rochleder first supposed it to be $C^{16}H^{18}O^8$, but afterwards gave the preference to $C^{14}H^{16}O^7$. Gerhardt (Traité, iii. 886) suggested $C^{35}H^{38}O^{17}$, according to which caffetannic acid would be a homologue of gallotannic acid, $C^{27}H^{22}O^{17}$, differing from it by $8CH^2$. Pfaff supposes it contains two acids, *caffeic* and *caffetannic*; but Rochleder found only one, viz. caffetannic acid, with traces of citric acid.

The *caffetannates* are but little known. The *potassium*-salt is amorphous, soluble in water, insoluble in alcohol, and turns brown from oxidation on exposure to the air. The *barium*- and *calcium*-salts are yellow, and quickly turn green on exposure to the air. The *lead*-salt is a white precipitate of very variable composition.

The *caffetannate of caffeine and potassium*, prepared as already described (p. 706), forms spheroïdal groups of crystals, which become electric by friction. They are very soluble in water, less soluble in aqueous alcohol, nearly insoluble in absolute alcohol. The aqueous solution turns brown when exposed to the air. They are decomposed by dry distillation, swelling up strongly and yielding a sublimate of caffeine. Gently heated with potash, they assume a red or orange colour. Heated with strong sulphuric acid, they yield a liquid of deep violet colour, with a bronze pellicle on the surface. Nitric acid colours them orange-yellow.

CAÏNCIC ACID. $C^{16}H^{26}O^7$ (?) (François, Pelletier, and Caventou, 1830, J. Pharm. xvi. 465.—Liebig, Ann. Ch. Phys. [2] xlvii. 185.—Rochleder and Hlasiwetz, Ann. Ch. Pharm. lxxvi. 238.—Gerh. Traité, iii. 746.)—Found in the root of caïnca (*Chiococca anguifuga*, Martius), a rubiaceous plant growing in Brazil, and used as a remedy against the bites of serpents; also in the root of *Chiococca racemosa* (*L.*), a plant much used in the Antilles for the cure of syphilis and rheumatism.

It is prepared: 1. By exhausting caïnca root with alcohol, concentrating the alcoholic extract, mixing it with water, and adding milk of lime to the filtered liquid till it loses its bitterness. An insoluble basic caïncate of calcium is thus produced, which is decomposed by a hot alcoholic solution of oxalic acid. The filtered solution, when evaporated, yields caïncic acid in shining needles (Pelletier and Caventou).—2. From the root of *Chiococca racemosa*, by exhausting the bark of that root with alcohol; mixing the solution with neutral acetate of lead, which throws down caffetannate of lead, together with some caïncate and phosphate; then treating the filtrate with subacetate of lead, which forms a yellow precipitate containing the greater part of the caïncic acid, with only traces of caffetannic acid. This precipitate being decomposed by sulphuretted hydrogen, and the filtrate sufficiently concentrated, the caïncic acid is deposited in crystalline flakes, which may be purified by crystallisation from boiling water containing a little alcohol.

Caïncic acid is inodorous; tasteless at first, afterwards very bitter; sparingly soluble in water and ether, very soluble in alcohol. Reddens litmus perceptibly. The crystals give off 9 per cent. water at 100° C. (Liebig). When heated it softens, chars, and yields a crystalline sublimate which is not bitter. Dilute acids and strong alkalis convert it into quinovatic acid.

The *caïncates* are but little known; they have a bitter taste. The neutral caïncates of *ammonium*, *potassium*, *barium*, and *calcium* are soluble in water, deliquescent, and uncrystallisable. Lime-water, added to the solution of neutral caïncate of calcium, produces a copious precipitate of a basic salt, soluble in boiling alcohol, whence it separates in white flakes, which are strongly alkaline. The *normal lead-salt*, $C^{16}H^{24}Pb^2O^7 + H^2O$, is precipitated on mixing strong alcoholic solutions of caïncic acid and acetate of lead. There are also basic lead-salts.

CAIRNGORM STONE. Smoky quartz. See QUARTZ.

CAJEPUT, OIL OF. This oil is prepared in India by distilling the leaves of *Melaleuca Leucodendron* (*L.*) with water. It was formerly employed to a great extent in medicine, both internally and externally, but is now but little used, and is seldom met with in a pure or unchanged state, except in the hands of wholesale druggists. As introduced into Europe, it possesses a light green colour, resembling that of a dilute solution of chloride of chromium, which is caused by a resinous colouring matter dissolved in it in very small quantity.

The colour of the crude oil is also partly due to copper, the presence of which may be accounted for, either by the use of a copper head in the distilling apparatus of the Hindoos, or by intentional adulteration, resorted to for preserving the green colour of the oil, which otherwise changes gradually by oxidation to a reddish-brown, the oil then becoming unsaleable for medicinal purposes. That the oil possesses a green colour of its own is proved by the fact that the colour remains after the complete removal of the copper by sulphuretted hydrogen.

Oil of cajeput consists mainly of the dihydrate of a hydrocarbon called **cajputene**, isomeric with oil of turpentine. Its specific gravity is 0·926 at 10° C. On submitting it to fractional distillation, dihydrate of cajputene, which constitutes about two-thirds of the crude oil, passes over between 175° and 178° C.; smaller fractions, perhaps products of decomposition, are obtained from 178° to 240° and from 240° to 250°; and at

250° only a small residue is left, consisting of carbonaceous matter mixed with metallic copper. On treating this residue with ether, a green solution is obtained, which, when evaporated, leaves a green resin, soluble in the portion which boils between 175° and 178°, and capable of restoring the original colour. (M. Schmidl, Trans. Roy. Soc. Ed. xxii. [6] 360; Chem. Soc. Qu. J. xiv. 63.)

CAJPUTENE. $C^{10}H^{16}$. (Schmidl, *loc. cit.*)—This compound is obtained, together with two isomeric hydrocarbons, isocajputene and paracajputene, by cohobating dihydrate of cajputene with phosphoric anhydride for half an hour, and then distilling off the liquid, whereupon cajputene passes over at 160°—165° C.; isocajputene at 176°—178°, and paracajputene at 310°—316°.

Cajputene is permanent in the *air*. It is not affected by *iodine* at ordinary temperatures, but at a higher temperature, hydrogen is evolved and a black liquid is formed. *Bromine* acts quickly on it, producing a dark viscid oil. With *gaseous hydrochloric* acid, it forms a beautiful violet liquid, but no crystalline compound, even at −10° C. A mixture of ordinary *nitric* and *sulphuric acids* acts upon it with violence, forming a yellow bitter resin.

Cajputene is insoluble in *alcohol*, but dissolves in *ether* and in *oil of turpentine.*

Isocajputene, $C^{10}H^{16}$.—Obtained: 1, as above.—2, by distilling the dihydrate of cajputene with oil of vitriol. It is an oil boiling between 176° and 178° C. Its odour is less agreeable than that of cajputene, and becomes more pungent and aromatic by exposure to the air, the oil at the same time acquiring a yellow colour. Specific gravity = 0·857 at 16° C. Vapour-density of (1) = 4·82; of (2) = 4·52.

Iodine, bromine, gaseous hydrochloric acid, and a mixture of *nitric* and *sulphuric acids*, act upon isocajputene in the same manner as on cajputene. With *oil of vitriol*, and with *dilute sulphuric, hydrochloric*, or *nitric acid* (neither of which acts upon cajputene), it forms dark viscid liquids.

Isocajputene is insoluble in *water* and in *alcohol*, but mixes in all proportions with *ether* and with *oil of turpentine.*

Paracajputene, $C^{20}H^{32}$, obtained as above mentioned, by distilling dihydrate of cajputene with anhydrous phosphoric acid, passes over between 310° and 316° C. It is very viscous, has a lemon-yellow colour, and in certain directions exhibits deep-blue fluorescence. Vapour-density, by experiment = 7·96; by calculation (2 vol.) = 9·43. The difference between the experimental and calculated vapour-densities is probably due to decomposition, taking place at the high temperature required for the determination.

Paracajputene oxidises rapidly in contact with the *air*, acquiring a red colour and resinous consistence. A mixture of *nitric* and *sulphuric acids* does not act so violently on it as on cajputene and isocajputene. With *hydrochloric acid gas*, it forms a dark viscid liquid, which does not yield crystals, even at −10° C. It is insoluble in *water, alcohol*, and *oil of turpentine*, soluble in *ether.*

BROMIDE OF CAJPUTENE, $C^{10}H^{16}Br^4$.—Obtained by the action of bromine on oil of cajeput. When dry bromine is dropped into the rectified oil, a very brisk action takes place, and the sides of the vessel become covered with yellow needles, which however soon disappear; but if the addition of the bromine be continued till the reaction almost ceases, a dark, thick, viscous oil is formed, which, after several weeks, deposits a granular substance. By boiling the mixture with alcohol, the granular substance is extracted; a heavy oil is left behind; and the alcoholic solution, on cooling, deposits bromide of cajputene as a soft crystalline substance having a fatty lustre and much resembling cholesterin.

Bromide of cajputene melts at 60° C. and solidifies again at 32°. By dry distillation, it yields a liquid which crystallises again in the cooler parts of the retort. It is not altered by boiling with aqueous potash. It dissolves in ether and in boiling alcohol.

Rectified oil of cajeput shaken up with bromine-water, forms a red resin, from which a solid substance separates in small white prisms, extremely deliquescent and rapidly decomposing.

Another crystallised bromine-compound (probably a hydrobromate analogous to the hydriodate) is formed in the same manner as that compound (p. 713).

CHLORIDE OF CAJPUTENE, $C^{10}H^{16}Cl^2$, is produced by the action of nascent chlorine on the dihydrate (rectified cajeput oil). When the portion of the oil distilling between 175° and 178° C. is mixed with very dilute nitric acid, and hydrochloric acid gas is passed into the liquid, a violent action takes place in a few minutes, chlorine and nitrous gas being evolved; and, if the passage of the gas be continued, chloride of cajputene ultimately sinks to the bottom, as a limpid brown oil, which may be freed from adhering nitric and nitrous acid by distillation over strong potash-ley. It has a fragrant odour, and may be kept without alteration for any length of time, but is decomposed by distillation. Boiled with nitrate of silver, it detonates in a peculiar manner, and forms chloride of silver.

Hydrates of Cajputene. *Hemi-hydrate*, $C^{20}H^{34}O = (C^{10}H^{16})^2.H^2O$ (or perhaps *monohydrate of paracajputene*, $C^{20}H^{32}.H^2O$.)—Obtained by the action of oil of vitriol on oil of cajeput. When the crude oil is raised to the boiling-point in a deep open vessel, and oil of vitriol continuously dropped into it, violent ebullition takes place, accompanied, after a while, by a peculiar crackling sound. As soon as this is observed, the flame must be lowered and the acid very cautiously added, till the liquid suddenly assumes a dark colour, extending in an instant from the surface throughout the whole depth. The vessel must then be immediately removed from the fire, otherwise further decomposition will take place, attended with evolution of sulphurous anhydride. The upper oily liquid is separated from the acid on which it floats, well washed, and distilled, and the portion which passes over from the 170° to 175° is collected and rectified. It is an oily liquid, whose vapour-density, as found by experiment, is 5·19 to 5·27. Now the formula, $C^{20}H^{34}O$, if supposed to represent 2 volumes of vapour, gives for the calculated vapour-density the number 10·04 ($= \frac{240 + 34 + 16}{2} \times 0·0693$), which is nearly double the experimental number. Consequently, the molecule $C^{20}H^{34}O$ represents 4 volumes of vapour, and probably splits up at high temperatures into $C^{20}H^{32}$ and H^2O, each of which occupies 2 volumes. (See Atomic Weights, p. 469.)

Monohydrate. $C^{10}H^{18}O = C^{10}H^{16}.H^2O$.—This is the chief constituent of oil of cajeput (p. 710), and passes over in the fractional distillation between 175° and 178° C. After rectification, it is a colourless oil which boils constantly at 175°, has a specific gravity of 0·903 at 17° C., and vapour-density, by experiment = 5·43; by calculation (2 vol.) = 5·338. It dissolves in all proportions in *alcohol*, *ether*, and *oil of turpentine*.

Exposed to the *air* for a considerable time, in the moist state, it changes to a reddish liquid, which ultimately exhibits a rather strong acid reaction with litmus. *Iodine* dissolves in the oil, and under certain circumstances forms crystalline compounds (p. 712). *Bromine* acts quickly upon it, and under similar circumstances forms crystalline compounds (p. 711). *Chlorine gas* passed into the oil raises the temperature, but does not appear to act upon it further; but *nascent* chlorine (evolved by passing hydrochloric acid gas into the oil mixed with dilute nitric acid) converts it into dichloride of cajputene, $C^{10}H^{16}Cl^2$. *Phosphoric anhydride* heated with the monohydrate takes away the whole of its water, converting it into cajputene, isocajputene, and paracajputene (p. 711). *Chloride of zinc* likewise dehydrates it, but less completely. *Strong sulphuric acid* acts but very slowly on the oil at low temperatures; but if the temperature be allowed to rise, sulphurous anhydride is given off, and the oil blackens and ultimately suffers complete decomposition. If the action be checked at a certain point, a sulpho-acid is formed, which yields a soluble barium-salt. Oil of vitriol dropped into the oil at the boiling heat, in the manner above described takes away half the water, forming monohydrate of cajputene. *Dilute sulphuric acid*, on the contrary, causes the monohydrate to take up 2 at. more water, converting it into $C^{10}H^{16}.3H^2O$. *Fuming sulphuric acid* converts the monohydrate into a thick brown liquid, which boils above 360°. *Fuming nitric acid* rapidly oxidises the oil, even at ordinary temperatures, forming a large quantity of oxalic acid. Ordinary nitric acid produces the same effect at the boiling heat, but at ordinary temperatures it acts very slowly, converting the oil into a red liquid. Distilled over *permanganate* or *acid chromate of potassium* in presence of sulphuric acid, it forms a thick resinous liquid. It does not appear to be altered by digestion with *peroxide of lead*. In contact with aqueous *potash*, or when dropped into melting potash, it forms a soluble salt, the acid of which is precipitated as a resin by hydrochloric or sulphuric acid. Heated with *sodium*, it forms a crystalline mass, soluble in water and alcohol, and consisting of soda and an organic substance, which is separated by strong acids in the form of a fragrant resin. When the vapour of the monohydrate is passed over red-hot *soda-lime*, a yellow oil distils over, having a peculiar odour quite different from that of the monohydrate; at the same time the soda-lime becomes blackened by deposited charcoal, and when treated with acids, gives off a large quantity of carbonic anhydride. The yellow oil thus formed yielded by distillation, a fraction boiling between 180° and 185° C. which gave in two analyses, 79·76 and 80·03 per cent. C, 12·20 and 12·07 H, agreeing nearly with the formula $C^{26}H^{24}O^{2}$, which requires 79·59 per cent. C, 12·24 H, and 7·97 O.

Trihydrate of Cajputene, $C^{10}H^{22}O^3 = C^{10}H^{16}.3H^2O$.—Produced by the action of dilute sulphuric acid on the monohydrate, or on crude oil of cajeput. Two pts. of dilute sulphuric acid are added to 1 pt. of the crude oil; and the mixture is well shaken for several days till the watery liquid acquires a yellowish colour, and then left to itself for about ten days, whereupon it deposits crystalline tufts of the trihydrate, adhering to the sides of the vessel. The crystals melt at 120° C. and solidify again at

85°. On submitting them to dry distillation, an oily liquid passes over and condenses again in the colder parts of the apparatus, apparently as the unaltered trihydrate. The crystals dissolve sparingly in cold, easily in boiling alcohol.

Crystals having the same composition were deposited from a secondary fraction of crude cajeput-oil, which distilled at 210°—230° C., and was left for a very long time moist and exposed to the air. The crude oil mixed with nitric acid and alcohol, changes, in the course of seven or eight months, into a black heavy liquid in which crystals are suspended, perhaps consisting of the trihydrate. The same compound appears likewise to be formed in beautiful long prisms, when the crystalline mass produced by passing hydrochloric acid gas into rectified oil of cajeput is thrown into water or alcohol.

HYDROCHLORATES OF CAJPUTENE.—The *monohydrochlorate*, $C^{10}H^{16}.HCl$, is obtained by distilling the dihydrochlorate, and collecting apart the fraction which boils at 160° C. —A product having the same composition is obtained by treating the dihydrochlorate for several days with aqueous or alcoholic potash; but its odour is different from that of the product obtained by simple distillation of the hydrochlorate, and resembles that of pelargonic ether.

The *dihydrochlorate*, $C^{10}H^{16}.2HCl$, is obtained by passing hydrochloric acid gas through rectified cajeput-oil, mixed with a third of its volume of alcohol or strong aqueous hydrochloric acid. It crystallises from alcohol in beautiful radiating tufts; melts at 55° C. and solidifies again at 30°. It has no taste or smell. By dry distillation, it gives off hydrochloric gas at 60°, and splits into several fractions, one of which is the monohydrochlorate. It is also deprived of half its chlorine by heating with aqueous or alcoholic potash. It dissolves sparingly in cold, easily in boiling alcohol or ether.

HYDRIODATE OF CAJPUTENE. *a. Anhydrous.* $C^{10}H^{16}.HI$.—Obtained by adding a solution of phosphorus in sulphide of carbon to a solution of iodine and oil of cajeput in the same liquid. The liquid becomes hot, assumes a reddish colour, deposits red oxide of phosphorus, and gives off vapours, probably containing phosphoretted hydrogen, and after ten or twelve days deposits crystals of the hydriodate. The reaction is perhaps:

$$6(C^{10}H^{16}.H^2O) + 6PI = 6C^{10}H^{17}I + 2PH^3 + P^2O + P^2O^5.$$

The crystals are deposited in cells like those of beehives, and possess a black metallic lustre. They are soluble in alcohol and ether, and are very stable, not being altered even by boiling with potash.

b. Hydrated, $C^{20}H^{36}I^2O = 2(C^{10}H^{16}.HI).H^2O$, or *Hydriodate of Hemihydrated Cajputene*, $C^{20}H^{34}O.2HI$.—If iodine be added by small quantities, and with constant stirring, to cajeput-oil till the temperature rises from 10° to 40° C., and the vessel be then immersed in cold water, a black crystalline compound soon separates from it, and on filtering, pressing the black substance between paper, and then dissolving it in alcohol or ether, a solution is obtained, from which the hydrated hydriodate crystallises in prisms having a fine yellow-green colour and metallic lustre, and melting at 80° C. to a compound which does not recrystallise on cooling. Potash dissolves the crystals, abstracting part of the iodine in the cold, and the whole when heated. The crystals are insoluble in water, and are not decomposed thereby; they dissolve readily in alcohol and ether.

CALAITE. Syn. of TURQUOIS.

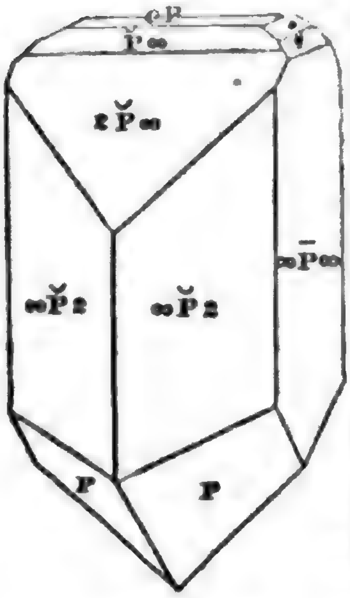
CALAMINE. *Native Carbonate of Zinc. Zinc-spar. Smithsonite. Galmei.* Zn^2CO^3. —This mineral, which is one of the most abundant ores of zinc, occurs crystallised in rhombohedrons with cleavage parallel to the rhombohedral faces. Ratio of principal to secondary axes = 0·8070 : 1. Inclination of terminal faces = 107° 40′. Also reniform, botryoïdal, and stalactitic, and in crystalline incrustations; likewise granular, earthy, and friable. Specific gravity = 4·45; hardness = 5. It is translucent or subtransparent; white when pure, but often tinged more or less with grey, green, or brown, from admixture of the carbonates of iron and manganese. Streak white. Lustre vitreous, inclining to pearly. Brittle, with uneven, imperfectly conchoïdal fracture.

Pure calamine is found in Somersetshire and Derbyshire. A specimen from Somersetshire analysed by Smithson (Nicholson's Journal, vi. 76) gave 35·2 per cent. CO^2, and 64·8 Zn^2O, which is exactly the theoretical composition. Generally, however, a portion of the zinc is isomorphously replaced by iron, manganese, calcium, magnesium, lead, and copper. The following are examples: *a.* From Nertzchinsk in Siberia, analysed by Kobell (J. pr. Chem. xxviii. 480.) *b, c, d.* From Altenberg near Aix-la-Chapelle (Monheim, Rammelsberg's *Mineralchemie*, s. 227.) *e, f.* From Herrenberg near Nirm, Aachen (Monheim, *ibid.*) *g.* A cupriferous variety called Herrerite, from Albarradon in Mexico. (Genth, Sill. Am. J. ii. xx.; J. pr. Chem. lxvi. 475.)

	Zn^2CO^3	Fe^2CO^3	Mn^2CO^3	Ca^2CO^3	Mg^2CO^3	Pb^2Co^3	Cu^2CO^3	SiO^2	Zn^2SiO^4	H^2O	
a . .	96·00	2·03	—	—	—	1·12	—	—	—	—	= 99·15
b . .	60·35	32·31	4·02	1·90	0·14	—	—	—	2·49	—	= 101·11
c . .	55·89	36·46	3·47	2·27	—	—	—	—	0·41	—	= 98·50
d . .	84·92	1·58	6·80	1·58	2·84	—	—	—	1·85	—	= 99·57
e . .	85·78	2·24	7·62	0·98	4·44	—	—	0·09	—	trace	= 101·15
f . .	74·42	3·20	14·98	1·68	3·88	—	—	0·20	—	0·56	= 98·92
g . .	93·74	—	1·50	1·48	0·29	—	3·42	—	—	—	= 100·43

CALAMINE, SILICEOUS. *Siliceous oxide of zinc. Hydrous silicate of zinc. Zinc-glance. Kieselzinkerz. Kieselgalmei.* $Zn^4SiO^4 + H^2O$.—(Dana applies to this mineral the name *calamine*, distinguishing the preceding as *Smithsonite.*) Occurs in crystals of the trimetric system. Ratio of brachydiagonal, macrodiagonal, and principal axis = 0·6385 : 1 : 0·6169. The crystals are short prisms (*fig.* 114) resulting from the predominance of the faces $\infty\breve{P}2$ and $\infty\bar{P}\infty$, and unsymmetrically terminated, viz. at one end by the faces P, and at the other by $2\breve{P}\infty$. $\bar{P}\infty$. 0P . $\frac{1}{3}\bar{P}\infty$ (*y*) and $\frac{1}{3}\breve{P}\infty$ (*x*). Inclination of faces, $\infty\breve{P}2 : \infty\breve{P}2 = 103° 53'$; $\frac{1}{3}\bar{P}\infty : \frac{1}{3}\bar{P}\infty = 51° 34'$; $\breve{P}\infty : \breve{P}\infty = 63° 20'$; $2P : 2P\infty = 101° 56'$. Cleavage perfect parallel to $\infty\breve{P}2$; somewhat less, parallel to $\breve{P}\infty$ (Kopp's *Krystallographie*, pp. 250, 264). The mineral likewise occurs in stalactitic, mammillary, botryoïdal, and fibrous forms; also massive and granular. Specific gravity 3·16—3·9. Hardness = 4·5—5. It is white when pure, sometimes blue, more or less coloured by oxide of iron. Transparent or translucent. Lustre generally vitreous. Streak white. Brittle, with uneven fracture. Like many other unsymmetrical minerals, it is pyroelectric.

Fig. 114.



Before the blowpipe it melts with difficulty at the edges; it is not altered by heating on charcoal, either alone or with carbonate of sodium; but with carbonate of sodium and borax it is completely reduced, with formation of a zinc-deposit. It is easily decomposed by acids, with separation of gelatinous silica; it also dissolves in potash-ley.

Siliceous calamine generally occurs nearly pure. A specimen from Tarnowitz in Upper Silesia, analysed by Rammelsberg, yielded 24·99 SiO^2, 68·66 Zn^2O, and 7·75 H^2O = 101·40; the formula $Zn^4SiO^4 + H^2O$ or $2Zn^2O.SiO^2 + H^2O$, requiring 25·1 SiO^2, 67·4 Zn^2O, and 7·5 H^2O. Sometimes a small portion of the zinc is partly replaced by iron or lead: in a specimen from Nertzschinsk in Siberia, Hermann found 2·70 per cent. oxide of lead.

Siliceous calamine usually occurs, associated with the native carbonate, in calcareous rocks. Large crystals are found at Nertzchinsk. (Dana, ii. 314; Rammelsberg's *Mineralchemie*, s. 549.)

CALAMITE. A variety of tremolite (*q. v.*) having an asparagus-green colour.

CALCAREOUS SPAR. See CALCSPAR.—**CALCEDONY.** See CHALCEDONY.

CALCHANTUM. Pliny's term for copperas.

CALCINATION. The fixed residues of such matters as have undergone combustion are called cinders in common language, and calces, or oxides, by chemists; and the operation, when considered with regard to these residues, is termed calcination. In this general way it has likewise been applied to bodies not really combustible, but only deprived of some of their principles by heat. Thus we hear of the calcination of chalk, to convert it into lime, by driving off its carbonic acid and water: of gypsum or plaster stone, of alum, of borax, and other saline bodies, by which they are deprived of their water of crystallisation; of bones, which lose their volatile parts by this treatment; and of various other bodies. (See COMBUSTION.)

CALCITE. Syn. with CALCSPAR (p. 721).

CALCIUM. *Symbol*, Ca. *Atomic weight*, 20.—Lime, the oxide of calcium, has been known from the earliest times, and was used by the ancients in the composition of mortar. Black, in 1756, first pointed out the difference between burnt and unburnt lime. The metal was first incompletely isolated by Davy in 1808, and has recently been obtained in the pure state by Matthiessen.

Calcium is the most widely diffused of the alkaline-earthy metals. The carbonate occurs in a great variety of forms, and, as limestone, constitutes entire mountain ranges. The sulphate, fluoride, phosphate, and silicate are also abundant natural products. Less frequent are the chloride, nitrate, arsenate, and tungstate. Calcium also exists as carbonate and phosphate in the bones of animals; the shells of molluscs are almost entirely composed of the carbonate. In the bodies of plants, calcium exists in combination with various organic acids.

Preparation of the Metal.—Davy in 1808 obtained calcium in an impure state by electrolysis, similarly to barium (p. 500), and by passing vapour of potassium over red-hot lime (?) Matthiessen (Chem. Soc. Qu. J. viii. 28) prepares the pure metal as follows:—A mixture of 2 at. chloride of calcium and 1 at. chloride of strontium, with a small quantity of chloride of ammonium (this mixture being more fusible than chloride of calcium alone), is melted in a small porcelain crucible, in which a carbon positive pole is placed, while a thin harpsichord wire wound round a thicker one, and dipping only just below the surface of the melted salt, forms the negative pole. The calcium is then reduced in beads, which hang on to the fine wire, and may be separated by withdrawing the negative pole every two or three minutes, together with the small crust which forms round it. A surer method, however, of obtaining the metal, though in very small beads, is to place a pointed wire so as merely to touch the surface of the liquid; the great heat evolved, owing to the resistance of the current, causes the reduced metal to fuse and drop off from the point of the wire, and the bead is taken out of the liquid with a small iron spatula. Or, thirdly, the disposition of the apparatus may be the same as that for the reduction of strontium (*q. v.*)

Liès-Bodart and Gobin (Compt. rend. xlvii. 23) prepare calcium by igniting the iodide with an equivalent quantity of sodium in an iron crucible, having its lid screwed down. According to Dumas (Compt. rend. xlvii. 175) it is essential that the process be conducted in a closed vessel, as, under the ordinary atmospheric pressure, the sodium burns away, and the iodide of calcium remains unaltered.

Properties.—Calcium is a light yellow metal, of the colour of gold alloyed with silver; on a freshly cut surface the lustre somewhat diminishes the yellow colour, which becomes more apparent when the light is reflected several times from two surfaces of calcium, or when the surface is slightly oxidised. It is about as hard as gold, very ductile, and may be cut, filed, or hammered out into plates having the thickness of the finest paper. Its specific gravity is 1·5778. In dry air the metal retains its colour and lustre for a few days, but in damp air the whole mass is slowly oxidised. Heated on platinum-foil over a spirit-lamp, it burns with a very bright flash. It is not quickly acted on by dry chlorine at ordinary temperatures; but when heated, it burns in that gas with a most brilliant light; also in iodine, bromine, oxygen, sulphur, &c. With phosphorus, it combines without ignition, forming phosphide of calcium. Heated mercury dissolves it as a white amalgam. Calcium rapidly decomposes water, and is still more rapidly acted on by dilute nitric, hydrochloric, and sulphuric acids, nitric acid often causing ignition. Strong nitric acid does not act upon it below the boiling heat. In the voltaic circuit, with water as the liquid element, calcium is negative to potassium and sodium, but positive to magnesium. It is not, however, reduced by potassium or sodium from its chloride by electrolysis. On the contrary, a fused mixture of $CaCl$ with KCl or $NaCl$, in certain proportions, yields potassium or sodium, when subjected in a certain manner to electric action; hence it appears that the metal formerly obtained by reducing chloride of calcium with potassium or sodium, could not be calcium, but was probably a mixture of potassium or sodium with aluminium, silicon, &c. (Matthiessen.)

Calcium unites with all the non-metallic elements, forming compounds into which it enters for the most part as a monatomic radicle, *e. g.* the chloride $CaCl$, the oxide Ca^2O, the sulphide Ca^2S, &c. Most of the compounds are colourless; they have an acrid taste, and a lower specific gravity than the corresponding compounds of barium and strontium. Of the compounds of calcium with other metals, little is known, excepting that it forms an amalgam with mercury.

CALCIUM, BROMIDE OF. $CaBr$.—Formed by the direct union of calcium and bromine, or by dissolving lime or the carbonate in hydrobromic acid. The solution yields by evaporation colourless silky needles of the hydrated bromide, from which the anhydrous bromide may be obtained by heating. It is deliquescent and very soluble in alcohol.

CALCIUM, CHLORIDE OF. $CaCl$.—This compound exists in sea-water, river-water, and spring-water, and is produced by passing chlorine over red-hot lime, or better by dissolving lime or the carbonate in hydrochloric acid, and evaporating. It is also produced in large quantity in the preparation of ammonia by heating sal-ammoniac with slaked lime:

$$NH^4Cl + CaHO = CaCl + NH^3 + H^2O.$$

The residue is treated with water; the solution, which is always alkaline, is neutralised with hydrochloric acid, and the residue evaporated to dryness.

The aqueous solution, when highly concentrated, deposits the hydrated chloride,

$CaCl.3H^2O$, in six-sided prisms with pyramidal summits. It has a bitter taste. The crystals give off 2 at. water when dried in vacuo, leaving the hydrate $CaCl.H^2O$, which retains the original form of the crystals, but is opaque, and has the appearance of talc (Graham). At 200° C. they part with the whole of their water, leaving the anhydrous chloride in the form of a white porous mass.

The anhydrous chloride melts at a low red heat. If it be then exposed to the sun's rays, it afterwards appears luminous in the dark; it was formerly called *Homberg's phosphorus*. When ignited in contact with the air, it is partially converted into oxide and carbonate of calcium. Hence the porous chloride dried at about 200° C. is better adapted for absorbing water in organic analysis (p. 228) than the fused chloride; the latter, containing lime, absorbs carbonic acid as well as water.

Anhydrous chloride of calcium is exceedingly greedy of water, and is one of the most deliquescent substances known. 100 pts. of it in powder exposed to an atmosphere saturated with moisture absorb 124 pts. of water in ninety-six days, more, therefore, than is required for complete deliquescence (Brandes, Schw. li. 433). The crystallised chloride also deliquesces rapidly, and dissolves in half its weight of water at 0° C., in one-fourth of its weight at 16°, and in every proportion of hot water. The solution of the anhydrous chloride in water is attended with considerable evolution of heat; but the hydrated chloride in dissolving lowers the temperature of the liquid. A mixture of crystallised chloride of calcium and snow produces a degree of cold sufficient to freeze mercury.

Both the anhydrous and the hydrated chloride dissolve readily in alcohol. 10 pts. of absolute alcohol at 80° C. dissolve 6 pts. of anhydrous chloride of calcium; and the solution when evaporated in vacuo, at the winter temperature, yields rectangular laminæ containing 59 per cent. of alcohol, agreeing with the formula $4CaCl.7C^2H^6O$. The alcohol in this compound appears to take the place of water of crystallisation. It likewise forms similar compounds with methylic and amylic alcohols.

Chloride of calcium combines with *ammonia*, forming the compound $CaCl.4NH^3$, it cannot, therefore, be used for drying gaseous ammonia. It unites also with *chromic acid* and with *acetate* and *oxalate of potassium*.

A solution of chloride of calcium boiled with slaked lime dissolves that substance, and the filtered solution deposits an *oxychloride of calcium*, $2CaCl.3Ca^2O + 15H^2O$, which is decomposed by pure water and by alcohol.

CALCIUM, DETECTION AND ESTIMATION OF. 1. *Reactions in the dry way.*—The hydrated chloride and a few other calcium-compounds, when heated in the blowpipe flame on platinum-wire, impart a red colour to the flame, similar to that produced by strontium-salts, but less intense. The colour disappears as soon as the salts are dehydrated, and is not produced at all if barium is likewise present. Alcohol burned on soluble calcium-salts exhibits a red flame tinged with yellow.

The spectrum of a flame in which a volatile calcium-compound is ignited, according to Bunsen and Kirchhoff's method (p. 214), is distinguished by a broad bright green line situated at about the confines of the green and yellow of the normal solar spectrum, and an intensely bright orange line situated nearer to the red end of the spectrum than the orange band of strontium, and about midway between the lines C and D of the solar spectrum. This reaction is best seen with the chloride, bromide, and iodide of calcium; the sulphate does not produce it till it has become basic, the carbonate exhibits it most distinctly after the carbonic acid has been expelled. Compounds of calcium with the non-volatile acids require to be decomposed, generally by hydrochloric acid. To obtain the reaction with silicates not decomposible by hydrochloric acid, a small quantity of the mineral in fine powder is mixed on a platinum plate with excess of fluoride of ammonium, and gently heated till all the fluoride is volatilised; the residue is then moistened with sulphuric acid, and the excess of that acid driven off. If the remaining substance be ignited in the flame as above, the characteristic spectra of the alkali-metals, if present, are first seen, and afterwards those of strontium and calcium. If only a trace of calcium is present, the bead must be held for a few minutes in the reducing flame of the blowpipe, then moistened with hydrochloric acid, and again ignited in the gas-flame.

2. *Reactions in the wet way.*—The bromide, chloride, iodide, nitrate, acetate, and many other organic salts of calcium are soluble in water; the carbonate, borate, phosphate, arsenate, and oxalate are insoluble, the sulphate sparingly soluble; all of them, however, except the sulphate, dissolve readily in nitric or hydrochloric acid.

In the aqueous solutions of calcium-salts, *potash* or *soda* produces a white gelatinous precipitate of hydrate of calcium, unless the solution is very dilute. *Ammonia:* no precipitate. *Neutral carbonates of alkali-metals:* white precipitate of carbonate of calcium, soluble with effervescence, in nitric, hydrochloric and acetic acids. *Acid carbonates of alkali-metals:* no precipitate in the cold; pulverulent precipitate on boiling, attended with escape of carbonic acid. *Sulphuric acid* and *soluble sulphates:* white precipitate of sulphate of calcium, unless the solution is very dilute; in that case, the precipitate appears on addition of alcohol, in which the sulphate of calcium is quite insoluble. *Oxalic acid* and *oxalate of ammonium:* white precipitate of oxalate of calcium, easily soluble in nitric or hydrochloric acid, but insoluble in acetic acid. *Sulphydric acid, alkaline sulphides, ferrocyanide of potassium, hydrofluosilicic acid:* no precipitate.

By these characters calcium in solution may be immediately distinguished from all other metals, except barium and strontium, and from these it may be distinguished by the greater solubility of its sulphate. A solution of sulphate of calcium gives a white precipitate immediately with a soluble barium-salt, and after a while with a salt of strontium.

3. *Quantitative Estimation.*—Calcium may be estimated either as carbonate or as sulphate. The best method of precipitating it, is in most cases by oxalate of ammonium, the oxalate being the least soluble of all the salts of calcium. If the solution contains an excess of any strong acid, such as nitric or hydrochloric acid, it must be neutralised with ammonia before adding the oxalate of ammonium, because oxalate of calcium is soluble in the stronger acids. The precipitate, after being washed with hot water and dried, is heated over a lamp, care being taken not to allow the heat to rise above low redness. It is thereby converted into carbonate of calcium containing 40·15 per cent. of calcium or 56·12 of lime.

If, however, the solution contains any acid which forms with lime a compound insoluble in water, phosphoric or boracic acid for example, this method of precipitation cannot be adopted; because, on neutralising with ammonia, the lime would be precipitated in combination with that acid, and would not be converted into oxalate on addition of oxalate of ammonium. In such a case, the calcium may be precipitated as sulphate by adding pure dilute sulphuric acid and alcohol. The sulphate, when dried, contains 41·25 per cent. of lime. From acid solutions of phosphate of calcium the metal may, however, be precipitated by oxalate of ammonium, with addition of acetate of ammonium, because oxalate of calcium is insoluble in acetic acid, which dissolves the phosphate with facility.

4. *Separation from other Elements.*—From the metals of the first group (p. 217) calcium is easily separated by sulphydric acid, from those of the second, by sulphide of ammonium.

From the *alkali-metals*, calcium is easily separated either by oxalate of ammonium, or by sulphuric acid and alcohol.

Calcium is separated from *barium* by precipitating both the earths as carbonates, dissolving the carbonates in nitric acid, evaporating to dryness, and digesting the residue in absolute alcohol, which dissolves nitrate of calcium, but not nitrate of barium. They may also be separated in this manner in the form of chlorides, but the separation is less complete, because chloride of barium is not quite insoluble in absolute alcohol.

From *strontium*, calcium is separated in the same manner, nitrate of strontium being likewise insoluble in absolute alcohol.

When baryta, strontia, and lime occur together, the baryta is first separated by hydro-fluosilicic acid; the strontia and lime in the filtrate are then converted into sulphates; these sulphates, after being weighed, are converted into carbonates, either by fusion with carbonate of sodium or by boiling with the aqueous solution of that salt; the carbonates weighed; and the quantities of strontium and calcium determined, as follows:—Let x be the weight of the strontium, y that of the calcium, s that of the sulphates and c that of the carbonates; then we have the equations:

$$\frac{Sr^2SO^4}{Sr^2}x + \frac{Ca^2SO^4}{Ca^2}y = s; \qquad \frac{Sr^2CO^3}{Sr^2}x + \frac{Ca^2CO^3}{Ca^2}y = c.$$

$$\text{or } \frac{183\cdot8}{97\cdot8}x + \frac{136}{40}y = s; \qquad \frac{157\cdot8}{97\cdot8}x + \frac{100}{40}y = c.$$

Or, the carbonates may be dissolved in nitric acid, and the nitrates separated by absolute alcohol, as above.

5. *Atomic Weight of Calcium.*—Dumas found that 100 pts. of Iceland spar, $Ca^2O.CO^2$, yielded by calcination 56 pts. lime, Ca^2O, whence (since $CO^2 = 44$) the atomic weight of lime = 56, and that of calcium 20. Erdmann and Marchand, and likewise Berzelius, in repeating this mode of estimation, found for calcium the number 20·03. Berzelius (Traité, iv. 538) by converting pure lime into the sulphate, found Ca = 20·13. Lastly, Dumas (Ann. Ch. Pharm. cxiii. 33) has determined this number by decomposing pure chloride of calcium with nitrate of silver. White marble was treated with dilute hydrochloric acid; the solution mixed with excess of lime (prepared from the same marble); the filtrate evaporated; the residue again treated with hydrochloric

acid, and ignited in hydrochloric acid gas; and the pure chloride of calcium thus obtained was decomposed by nitrate of silver. Three experiments thus made gave respectively $Ca = 20{\cdot}00$, $20{\cdot}03$, $20{\cdot}00$. The number 20 is generally adopted.

CALCIUM, FLUORIDE OF. CaF.—This compound occurs abundantly in nature, sometimes massive, sometimes crystallised in octahedrons, cubes, and other forms of the regular system (see FLUOR-SPAR). It is peculiarly a constituent of metalliferous veins. In minute quantity it is very generally diffused, being associated, to the amount of a few thousandths, with phosphate of calcium, in the bones of animals, and in somewhat larger quantity in the enamel of the teeth; minute quantities of it also found in plant-ashes and in the earthy deposit formed in sea-water by boiling. It may be prepared artificially as a gelatinous mass, by precipitating a soluble calcium-salt with fluoride of potassium or sodium, or in the granular state, by neutralising hydrofluoric acid with carbonate of calcium.

Fluoride of calcium dissolves in about 2000 pts. of water at 15° C. (G. Wilson), and somewhat more abundantly in water containing carbonic acid; hence its occurrence in sea-water. It dissolves in free hydrofluoric acid and in strong hydrochloric acid, and is precipitated as a transparent jelly by ammonia. It melts at a high temperature, and crystallises on cooling. It is decomposed at a high temperature by vapour of water, yielding lime and hydrofluoric acid. Fused with hydrate or carbonate of potassium, or sodium, it yields oxide or carbonate of calcium and an alkaline fluoride. Strong sulphuric acid does not decompose it at ordinary temperatures, but on heating the mass, hydrofluoric acid is given off, and sulphate of calcium remains. Vapour of sulphide of carbon passed over a red-hot mixture of fluor-spar and charcoal at a red heat, decomposes the fluoride completely, forming sulphide of calcium and volatile fluorine-compounds. It is also decomposed at a red heat by chlorine. (Frémy.) (See FLUORINE.)

Fluor-spar is much used as a flux in metallurgic operations, especially in the treatment of copper ores; also in the reduction of aluminium (p. 151).

CALCIUM, IODIDE OF. CaI.—Prepared by heating calcium in iodine vapour or by dissolving lime or the carbonate in hydriodic acid, evaporating and fusing the residue in a closed vessel. Resembles the chloride, melts below a red heat, and if in contact with the air, is decomposed, with formation of lime and separation of iodine. Very soluble and deliquescent. Decomposed by sodium at a red heat. The hydrate crystallises in long needles.

CALCIUM, OXIDE OF. *Lime*, Ca^2O, or CaO.—Anhydrous or quick lime is obtained by heating to redness the carbonate, nitrate, or any salt of calcium containing an acid easily expelled by heat; but for actual preparation, the carbonate is the only salt employed. In a closed vessel capable of resisting pressure, carbonate of calcium may be melted without undergoing decomposition; but when heated to redness under the ordinary atmospheric pressure, it gives off carbonic anhydride and leaves lime ($Ca^2CO^3 = Ca^2O + CO^2$). On the small scale, the decomposition may be performed in a crucible heated in a furnace; to obtain perfectly pure lime, the crystallised carbonate or the finest Carrara marble should be used. On the large scale, masses of limestone are burned in kilns, the mineral being mixed up with the coal or other combustible matter. In general, one bushel of coal is sufficient to make five or six bushels of lime; magnesian limestones require less fuel than pure limestone. When a limestone containing much aluminous or siliceous earth is to be burnt, great care should be taken to prevent the fire from becoming too intense; for such lime easily vitrifies. The kilns for burning these argillaceous or siliceous limestones should be provided with a damper. (See *Ure's Dictionary of Arts, Manufactures, and Mines*, ii. 729.)

Pure lime forms white hard porous masses of specific gravity 2·3 to 3·08. It bears the strongest heat without decomposition, and melts only in the flame of the oxyhydrogen blowpipe or in the voltaic arc. Its most remarkable property is the avidity with which it takes up water. When water is poured upon pure lime, it is instantly absorbed, and in a few seconds the lime becomes hot, gives off a large quantity of steam, and crumbles to powder: this is called the *slaking* of lime; with large masses the evolution of heat and escape of vapour are very violent. Lime which slakes easily, is called *fat lime*. Impure lime, especially that which contains clay, takes up water but slowly: such lime is said to be *poor*.

The product of the action of water on lime, is *hydrate of calcium* or *hydrate of lime*, $CaHO$ or $Ca^2O.H^2O$. It is a white soft powder, which gives off its water at a red heat, and is reconverted into quicklime. It is sparingly soluble in water, more in cold than in hot water: hence, water saturated with lime in the cold, deposits the hydrate when boiled. A solution evaporated in vacuo over oil of vitriol, deposits the hydrate in hexagonal prisms (Gay-Lussac). According to Dalton, lime-water formed at 60° 130°, and 212° (Fahr.) contains 1 grain of lime (anhydrous) in 778, 972, and 1270 grs.

of water. The solution, called *lime-water*, is alkaline, and has a caustic taste. It precipitates most metallic oxides from their solutions, all those in fact which are insoluble in water; also carbonic, boracic, silicic, and phosphoric acids when added to their neutral or alkaline solutions, or in excess to their acid solutions. When exposed to the air, it soon becomes covered with a pellicle of carbonate of calcium. The solid hydrate also absorbs carbonic acid from water, forming, according to Fuchs, the hydrocarbonate $Ca^2CO^3.HCaO$.

Lime dissolves readily in nitric, hydrochloric, and acetic acid. The hydrate exposed to the action of chlorine gas, forms a mixture of chloride and hypochlorite of calcium, commonly called *chloride of lime* or *bleaching powder:*

$$Ca^2O + Cl^2 = CaCl + CaClO.$$

Chlorine does not act upon anhydrous lime or on the carbonate.

Lime is applied to a variety of useful purposes: —1. For making mortar. The lime in the state of hydrate, is mixed with 2 pts. of coarse or 3 pts. of fine sand, and made with water into a paste, which as it dries, absorbs carbonic acid slowly from the air, and is converted into a hard mass of hydrate and carbonate, which binds the stones or bricks firmly together. The chief use of the sand is to prevent by its mass the too great contraction of the mortar in drying. — 2. In tanning, to promote the separation of the hair or wool from the skins, and of the fat and fleshy parts.—3. In the preparation of caustic alkalis from their carbonates. —4. In the saponification of fatty bodies intended for the preparation of stearine candles.—5. In the defecation of sugar (see SUGAR).—6. As a manure. Soils containing too much clay, are often mixed with lime, which, by absorbing water and carbonic acid, swells and disintegrates, and thus renders the soil lighter. It also exerts a decomposing action on the clay, rendering the silicate of potassium soluble.

Peroxide of Calcium, CaO, is known only as a hydrate, which falls down in very fine crystalline scales when lime-water is mixed with an aqueous solution of peroxide of hydrogen. (Thénard.)

CALCIUM, OXYCHLORIDE OF. (See page 716.)

CALCIUM, OXYGEN-SALTS OF. See the several ACIDS.

CALCIUM, OXYSULPHIDE OF. When sulphide of calcium prepared by reducing the sulphate with charcoal, is boiled with a large quantity of water, the solution filtered hot, and evaporated in a retort containing air, a large quantity of sulphuretted hydrogen escapes with the watery vapours: the cooled liquid deposits sulphite of calcium, and on further concentrating the mother-liquor, gold-coloured needles are obtained consisting of an oxysulphide $Ca^{12}S^5O + 20 aq$. When heated out of contact with the air, they give off water and sulphur, without alteration of form, and leave a white residue, which, when treated with hydrochloric acid, deposits sulphur, gives off sulphuretted hydrogen, and forms a product containing sulphate of calcium. (H. Rose, Pogg. Ann. xv. 433.)

CALCIUM, PHOSPHIDE OF. CaP or Ca^2P? — Prepared by passing vapour of phosphorus over red-hot lime. A good mode of proceeding is to place a few pieces of phosphorus at the closed end of a combustion-tube, fill the tube with small lumps of quick lime (made by forming slaked lime into pellets and calcining them), then heat the part of the tube containing the lime to redness, and pass the vapour of phosphorus over it by cautiously surrounding the closed end of the tube with hot fuel. To prepare larger quantities, a crucible having a hole at the bottom is filled with pellets of lime, and placed on the grate of a furnace, and a flask containing phosphorus is placed below the grating with its neck passing upwards through the hole in the crucible. The fire is then lighted, and as soon as the crucible is red-hot, the phosphorus in the flask is gradually heated, so that its vapour may pass upwards through the lime. The product is a brown mass consisting, according to Thénard, of hemiphosphide and pyrophosphate of calcium:

$$7Ca^2O + P^7 = 5Ca^2P + Ca^4P^2O^7.$$

According to Gmelin (Handb. iii. 188), it is a mixture of monophosphide and tribasic phosphate of calcium:

$$4Ca^2O + P^6 = 5CaP + Ca^3PO^4$$

Possibly both these reactions may take place together. The product, when thrown into water, is immediately decomposed, with evolution of spontaneously inflammable phosphoretted hydrogen:

$$3CaP + 3H^2O = PH^3 + 3CaHO + P^2;\ \text{or}\ 3Ca^2P + 3H^2O = 2PH^3 + 3Ca^2O + P.$$

Part of the diphosphide may also be decomposed in the manner represented by the equation:

$$Ca^2P + H^2O = PH^2 + Ca^2O.$$

The formation of the compound PH^2, may account for the spontaneous inflammability of the gas. (See PHOSPHORETTED HYDROGEN, under PHOSPHORUS.)

CALCIUM, SELENIDES OF. A *monoselenide* is formed by precipitating chloride of calcium with monoselenide of potassium; it is a flesh-coloured precipitate.

A *polyselenide*, mixed however with selenite of calcium, is produced by heating lime with selenium to a temperature just below redness. Lime-water saturated with seleniuretted hydrogen, deposits crystals of [mono ?] selenide of calcium when exposed to the air.

CALCIUM, SULPHIDES OF. The *monosulphide*, Ca^2S, is prepared: 1. By decomposing the sulphate with charcoal or coal.—2. By decomposing the sulphate at a red heat with carbonic oxide: $Ca^2SO^4 + 4CO = Ca^2S + 4CO^2$. — 3. By passing sulphuretted hydrogen over red-hot lime, water being formed at the same time. It is white, amorphous, with hepatic taste and alkaline reaction. It is but sparingly soluble in water: boiling water decomposes it, yielding sulphydrate and hydrate of calcium:

$$Ca^2S + H^2O = CaHS + CaHO.$$

Mixed with water, it is easily decomposed by carbonic acid, yielding carbonate of calcium and sulphydric acid:

$$Ca^2S + H^2O + CO^2 = Ca^2CO^3 + H^2S.$$

The monosulphide, after being heated, shines in the dark; it was formerly called *Canton's Phosphorus.*

Disulphide of Calcium, Ca^2S^2, is formed by boiling milk of lime with sulphur and water, but not long enough to allow the lime to be completely saturated. The filtered liquid on cooling, deposits crystals, whose composition agrees with the formula $Ca^2S^2.3H^2O$. (Herschell.)

Pentasulphide of Calcium, Ca^2S^5, is produced when the monosulphide or hydrate of calcium is boiled for a considerable time with excess of sulphur. It absorbs oxygen with avidity. When hydrate of calcium is used, there is also formed an oxysulphide represented by the formula $Ca^{12}S^5O.20H^2O$, or $5Ca^2S.Ca^2O.20H^2O$. (H. Rose.)

SULPHYDRATE OF CALCIUM, $CaHS$ or $Ca^2S.H^2S$, is formed, together with the hydrate, when the monosulphide is repeatedly boiled with water. The best mode of preparing it is to pass sulphuretted hydrogen through hydrate or sulphide of calcium suspended in a considerable quantity of water, as long as it is absorbed, stirring well all the while. The solution thus formed has a sharp, bitter, hepatic taste, an alkaline reaction, and slight causticity. The compound cannot be separated from it in the solid state, even by evaporation in vacuo or in hydrogen gas, being resolved, as soon as crystallisation begins, into sulphydric acid which escapes, and sulphide of calcium which separates in silky prisms. If the solution be boiled down in a retort containing air, sulphydric acid escapes and oxysulphide of calcium is deposited (p. 715).

Sulphydrate of calcium may be used as a depilatory, and is recommended for this application by Böttger (Ann. Ch. Pharm. xxix. 79), in place of sulphide of arsenic. It may be prepared for the purpose by passing sulphuretted hydrogen into thin milk of lime till the mass acquires a bluish-grey colour (from admixed sulphide of iron). The paste thus formed, is laid, to the thickness of a line, on the surface from which the hair is to be removed, and scraped off after a minute or two with a blunt knife, the hair then coming away with it. If it could be produced cheaply enough, it might be used for removing the hair from hides in the tan-yard.

CALC-SINTER. *Stalactitic carbonate of lime.* It is found in pendulous conical rods or tubes, mammelated, massive, and in many imitative shapes. Fracture lamellar, or divergent fibrous. Lustre silky or pearly. Colours, white of various shades, yellow, brown; rarely green, passing into blue or red. Translucent, semi-hard, very brittle. Large stalactites are found in the grotto of Antiparos, the Woodman's cave in the Harz, the cave of Auxelle in France, in the cave of Castleton in Derbyshire, and Macalister cave in Skye. They are continually forming by the infiltration of carbonated lime water, through the crevices of the roofs of caverns. Solid masses of stalactite have been called oriental alabaster. The irregular masses on the bottoms of caves are called stalagmites. U.

CALCOFERRITE. A yellow laminar mineral, from Battenberg in Rhenish Bavaria, containing, according to Reissig, 34·01 per cent. P^2O^5; 24·34 Fe^4O^3, 2·96 Al^4O^3, 14·81 Ca^2O, 2·65 Mg^2O, and 20·56 water (= 99·27), a composition agreeing nearly with the formula $2(2Ca^2O.P^2O^5).2Fe^4O^3.P^2O^5 + 12aq$. It exhibits perfect cleavage in one direction, and traces in two other directions, oblique to each other but perpendicular to the first, and is therefore probably orthorhombic. Specific gravity 2·52—2·53. Hardness = 2·5. Fuses readily before the blowpipe to a black, shining, magnetic globule. Dissolves easily in hydrochloric acid. (Handw. d. Chem. ii. [2] 671.)

CALCSPAR. *Calcareous Spar. Calcite.*—The rhombohedral form of carbonate of calcium. The primary form is an obtuse rhombohedron (*fig.* 116), in which the length of the principal axis to that of the secondary axis as 0·8543 to 1, and the angle of the terminal edges is 105° 5′. Of this, there are numerous modifications, among which are many acute and obtuse rhombohedrons, and likewise scalenohedrons, but all distinctly cleavable parallel to the faces of the primary rhombohedron. The primary form, + R, seldom occurs as an unbroken crystal in pure calcspar, but is the prevailing form of bitter-spar ($CaMgCO^3$). Most of the forms occur only in combination. The dimensions of the most frequently occurring rhombohedrons are given in the following table, each of them being the *next acuter* rhombohedron with relation to the one above, and *next obtuser* with relation to that next below it. (See CRYSTALLOGRAPHY, HEXAGONAL SYSTEM.)

	Principal axis.	Inclination of faces at terminal edges.	Inclination of faces at lateral edges.
+ $\frac{1}{4}$R	0·2136	156° 2′	23° 58′
− $\frac{1}{2}$R	0·4271	134° 57′	45° 3′
+ R	0·8543	105° 5′	74° 55′
− 2R	1·7086	78° 51′	101° 9′
+ 4R	3·4172	65° 50′	114° 10′

These forms, and combinations of them, are shown in figures 115, 116, 117, 118, 119, 120, 121. *Fig.* 115 is one of the most common of the rhombohedrons, and is frequently found alone, but still more frequently in combination with the hexagonal prism, producing the form seen in *fig.* 122. It occurs abundantly at Andreasberg in the Harz, and in the mines of Derbyshire. Among the scalenohedrons, is the variety called *Dog's-tooth spar*, + R^3 (*fig.* 123), in which the inclinations of the faces in the terminal edges are 104° 38′ and 144° 24′. It is found in Derbyshire and other localities. It frequently occurs also in hemitropic twin-crystals (*fig.* 124), which may be supposed to be formed by cutting the crystal (*fig.* 123), in halves by a horizontal plane, and turning one of the halves through an angle of 180°.

Fig. 115.

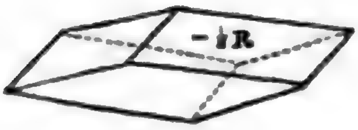


Fig. 116.

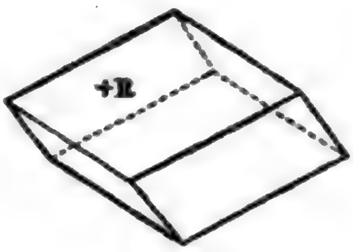


Fig. 117.

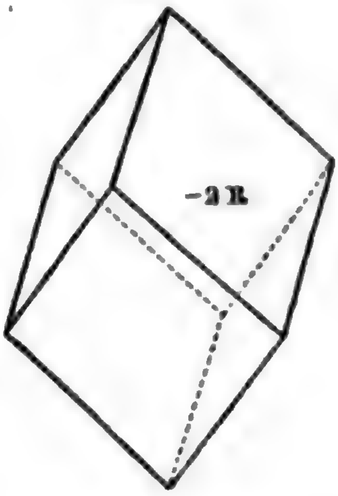


Fig. 118.

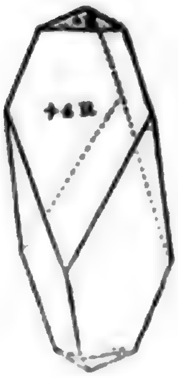


Fig. 119.

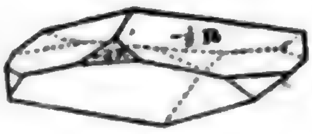


Fig. 120.

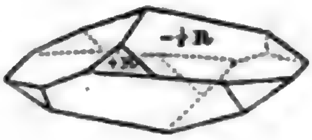
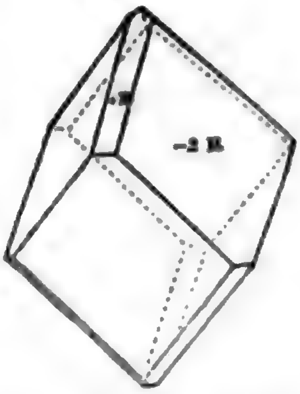


Fig. 121.



The specific gravity of the purest crystals of calcspar is 2·721. Hardness = 3, being intermediate between gypsum and fluorspar. Calcspar when pure is colourless, but often exhibits various tints of yellow, green, red, brown, and even black, arising from impurities. Lustre vitreous. Translucent more or less, and when transparent, exhibits in a remarkable degree, the double refraction of light. This property is best seen in the beautiful crystals obtained from Iceland, hence known as Iceland spar. These crystals exhibit the ground-form R, being in fact merely fragments of larger crystals.

Fig. 122.

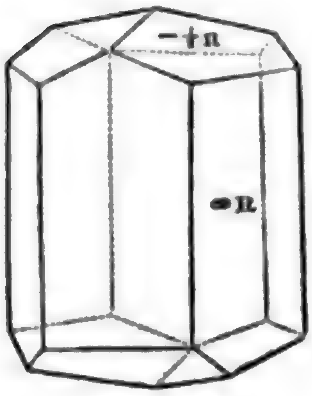


Fig. 123.

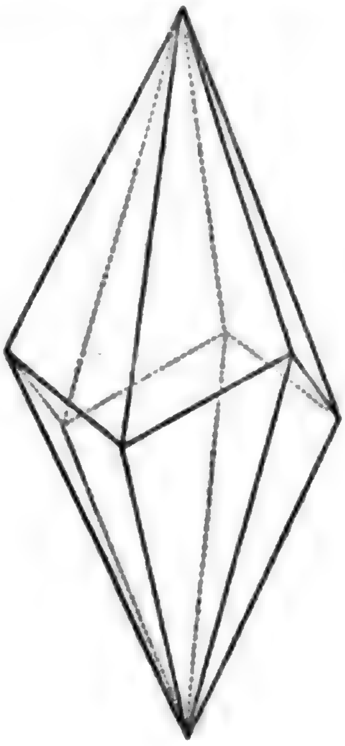
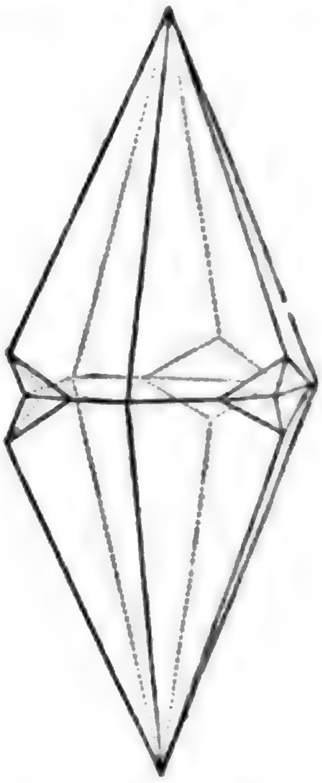


Fig. 124.



Calcspar occurs in all parts of the world, and is one of the most abundant of minerals. The lead-mines of Derbyshire and Cumberland, and of Andreasberg in the Harz, are noted as affording the most beautiful crystals and the greatest variety of form. [Respecting the circumstances under which carbonate of calcium assumes the forms of calcspar and of arragonite, see ARRAGONITE, p. 358.]

CALCTUFF. An alluvial form of carbonate of calcium, probably deposited from calcareous springs. It has a yellowish-grey colour, a dull lustre internally; a fine-grained earthy fracture; is opaque, and usually marked with impressions of vegetable matter. Its density is nearly the same as that of water. It is soft and easily cut or broken. U.

CALCULUS, or **STONE.** The name generally given to all hard concretions, not bony, formed in the bodies of animals. (See BEZOARS, BILIARY CALCULI, URINARY CALCULI.)

CALDERITE. A mineral from Nepal, said by Söchting (Deutsche geolog. Gesellschaft, ix. 4) to be a kind of garnet.

CALEDONITE. *Cupreous Sulphocarbonate of Lead*, from Leadhills in Scotland, consists, according to analyses by Brooke (Ed. Phil. J. iii. 117), and Thomson (Phil. Mag. 1840, p. 402), of $3Pb^2SO^4.2Pb^2CO^3.Cu^2CO^3$. It occurs in prismatic crystals of the trimetric system, with numerous secondary faces, sometimes large, but usually minute, and occasionally in branches diverging from a point. Specific gravity = 6·4. Hardness = 2·5—3. Colour verdigris- or bluish-green. Streak greenish-white. Lustre resinous. Translucent. Fracture uneven. Rather brittle. It is easily reduced before the blowpipe, and dissolves partially in nitric acid, with separation of sulphate of lead.

CALENDULIN. A mucilaginous substance extracted from the leaves and flowers of the common marigold, *Calendula officinalis*. (Geiger, *Diss. de Cal. off.*, Heidelberg, 1848.)

CALICO-PRINTING. The art of dyeing cloth (chiefly cotton and linen), topically; that is, impressing figures in one or more colours on certain parts of the cloth, while the rest of the surface is left in its original state. (See *Ure's Dictionary of Arts, Manufactures, and Mines*, i. 491.)

CALIFORNIN. A bitter principle extracted from *Chica Californica*. (Winckler, Buchn. Repert. xxxii. 20.)

CALISAYA BARK. See CINCHONA BARK.—**CALLAIS.** See TURQUOIS.

CALLUNA VULGARIS. An ericaceous plant, commonly called *Ling*. It contains, according to Rochleder, a peculiar tannic acid; the leaves and branches contain a trace of volatile oil, an acid, probably citric acid, and a small quantity of ericolin. 100 pts. of the air-dried plant yield, according to Sprengel, 1·95 ash (I.) Röthe found in the plant collected at the end of August, 5·55 per cent. water, and the dried plant yielded 6·35 per cent. ash (II.) Nutzinger found in the air-dried plant growing on moor-land, 2·87 per cent. ash (III.); and Thielau found in the flowering plant growing on the lias sand-stone, 3·32 per cent. ash (IV.) The ash contained in 100 pts:

	K^2O	Na^2O	Ca^2O	Mg^2O	Al^4O^3	Fe^4O^3	Mn^4O^3	Cl	SO^3	P^2O^5	SiO^2
I. . .	4·8	10·2	26·5	8·4	2·3	2·7	4·6	4·9	5·2	0·6	29·7
II. . .	10·6	0·8	12·0	6·7	—	4·9	4·1	—	1·7	10·9	48·1
III. . .	6·4	5·4	33·5	8·0	0·8	2·0	3·8	1·8	1·4	4·0	32·7
IV. . .	29·6		15·5	6·6	0·5	1·5	4·7	4·1	1·0	5·3	30·9

CALLUTANNIC ACID. $C^{14}H^{14}O^9$ or $C^{14}H^7C^9$ (Rochleder, Ann. Ch. Pharm. lxxxiv. 354).—The tannic acid of *Calluna vulgaris*. To obtain it, the alcoholic extract of the green parts of the plant (without the root) is mixed with water; the liquid filtered from a green precipitate of fat, chlorophyll, &c., is precipitated with acetate of lead; the washed precipitate treated with very dilute acetic acid, in which it is but partially soluble; the filtrate mixed with excess of sub-acetate of lead; the resulting yellow precipitate decomposed by sulphuretted hydrogen; and the filtered liquid evaporated on a chloride of calcium bath, in an atmosphere of carbonic anhydride. Callutannic acid then remains as an inodorous amber-coloured mass. This acid does not form any definite salts with the alkali-metals, alkaline-earth-metals or silver: for its solutions in alkalis or alkaline earths quickly absorb oxygen from the air, and oxide of silver is immediately reduced by it. Rochleder has obtained two lead-salts to which he assigns the formula $5PbO.HO.2C^{14}H^6O^8$ and $8PbO.2HO.3C^{14}H^6O^8$, and a stannic salt said to contain $7SnO^2.2HO.2C^{14}H^6O^8$.

Callutannic acid may be used to dye wool. The aqueous solution mixed with stannic chloride and a few drops of hydrochloric acid, and heated to the boiling point, imparts to wool mordanted with alum, a sulphur-yellow to chrome-yellow colour, according to the strength of the solution and the time of immersion.

CALLUXANTHIN. $C^{14}H^{10}O^7$.—A yellow flocculent substance obtained by boiling callutannic acid with dilute mineral acids. It is sparingly soluble in cold water, easily in hot water and in alcohol. It dissolves also in alkaline liquids, but the solution quickly absorbs oxygen, and is then precipitated by dilute acids in red-brown flocks. (Rochleder.)

CALOMEL. Hemichloride of mercury or mercurous chloride. See MERCURY.

CALOPHYLLUM RESIN. *Maynas resin*, $C^{14}H^{18}O^4$.—A resin from Maynas in South America, obtained from *Calophyllum Caloba* or *C. longifolium*. It has the aspect of common resin, dissolves in alcohol, ether, and oils, both fixed and volatile, and crystallises from boiling alcohol in small transparent colourless prisms of specific gravity 1·12. It melts at 105° C., but does not resolidify till cooled to 90°. It is decomposed by dry distillation; dissolves with red-brown colour in sulphuric acid, but is precipitated unaltered by water; and when heated with nitric acid of specific gravity 1·32, is said to yield butyric and oxalic acids, together with another acid which does not precipitate calcium-salts. With chromic acid, it is said to yield carbonic and formic acids. It dissolves in alkalis. (Levy, Compt. rend. xviii. 242.)

CALORIMETER. An instrument for the estimation of latent heat, specific heat, heat of combustion, &c. (See HEAT.)

CALORIMOTOR. A voltaic arrangement consisting of one pair or a few pairs of very large plates, used chiefly for producing considerable heat effects. (See ELECTRICITY.)

CALSTRONBARYTE. Shepard's name for a variety of heavy spar from Shoharie in New York, mixed with carbonate of strontium and calcium. (Sill. Am. J. xxxiv. 161.)

CALYPTOLITE. A mineral from Haddam and Mittletown in Connecticut, crystallised in square prisms of specific gravity 4·34, hardness 6·5. Probably an altered zircon. (Shepard, Sill. Am. J. [2] xii. 210.)

CAMBOLEY RESIN. A resin from *Morus indica*.

CAMELLIA JAPONICA. The leaves contain tannin, which is sparingly precipitated by gelatin, abundantly by lead and iron salts: they do not contain theine. (Stenhouse.)

CAMPEACHY WOOD. See LOGWOOD.

CAMPHAMIC ACID and **CAMPHAMIDE.** See CAMPHORAMIC ACID and CAMPHORAMIDE.

CAMPHENE. This term is used in various ways; sometimes as a generic name for the hydrocarbons isomeric or polymeric with oil of turpentine, sometimes as the name of the radicle of camphor ($C^{10}H^{16}$) and its allied compounds. By Dumas and Berthelot, it has been applied especially to the hydrocarbon, also containing $C^{10}H^{16}$, obtained by the action of alkalis on hydrochlorate of turpentine-oil. Laurent applied the same appellation to the radicle of oil of cloves, eugenin, &c.

Chlorinated and brominated derivatives of camphene, *e. g.* $C^{10}H^{14}Cl^2$ and $C^{10}H^{12}Br^4$ are obtained by the action of chlorine or bromine on oil turpentine and its isomers. A *monochlorocamphene*, $C^{10}H^{15}Cl$, and a *dichloride of camphene*, $C^{10}H^{16}Cl^2$, are produced by the action of pentachloride of phosphorus on camphor (see p. 728).

CAMPHENES or *Terebenes.* The generic name for the volatile oils or hydrocarbons $C^{5n}H^{8n}$, isomeric or polymeric with oil of turpentine. Most of them are isomeric and consist of $C^{10}H^{16}$, *e. g.* oil of turpentine, oil of lemons, oil of juniper, caoutchin, &c.; some, as colophene, appear to consist of $C^{20}H^{32}$.

Many camphenes exist ready formed in plants, as the oils of juniper, lemon, and turpentine; they are often contained in the natural oils associated with oxygenated compounds, and may be separated therefrom by fractional distillation, as carvene from oil of caraway, borneene or valerene from oil of valerian, &c. Many are produced from oxygenated compounds containing $C^{5n}H^{8n}$ + water, by the action of phosphoric anhydride (*e. g.* borneene from borneol, cinæbene from wormseed-oil, &c.) Others are formed from oxygenated oils by the action of hydrate of potassium (oil of sage and others); some by dry distillation, as oil of amber, caoutchin, &c.

All the camphenes are liquid at ordinary temperatures (except Berthelot's camphene, which is a solid melting at 46° C.); they have for the most part a density of 0·8 to 0·9 (oil of parsley is the only one heavier than water, specific gravity = 1·0 to 1·1), and boil between 155° and 165° C.; their observed vapour-density varies from 4·6 to 4·8, the formula $C^{10}H^{16}$ calculated for 2 vol. giving a thoretical density of 4·7. A few only boil at higher points, viz. oil of copaiba at 250° C.; petrolene at 280°; colophene at about 310°; cinæphene at nearly 320°, metaterebene about 360°. The observed vapour density of carvene is 5·1, of tolene 5·7, of petrolene 9·4, of colophene 11·1; the formula $C^{20}H^{32}$ calculated for 2 vol. requires 9·4.

Camphenes are distinguished one from the other by their odours, which in some, as oil of lemon, are very fragrant, in others, as in oil of copaiba, extremely disagreeable; also by their action on polarised light. All natural camphenes possess the optical rotatory power in a greater or less degree, some turning the plane of polarisation to the right, others to the left; but even in the same oil, the strength and direction of the rotatory power vary according to the temperature and other circumstances.

Camphenes readily absorb *oxygen* and convert it into ozone. *Iodine* for the most part decomposes them readily and with evolution of heat, sometimes even with slight explosion, the iodine taking the place of a portion of the hydrogen; this reaction serves to detect the admixture of camphenes, oil of turpentine, for example, with other volatile oils. *Chlorine* and *bromine* act in a similar manner.

Camphenes treated with *bromine* and *water* are easily converted into brominated oils (Gr. Williams, Phil. Mag. [4] v. 536). According to Chautard (Compt. rend. xxxiii. 671; xxxiv. 485), camphenes distilled with *water* and *bromide* or *chloride of lime*, yield, amongst other products, bromoform or chloroform.

Most camphenes unite with *hydrochloric acid*, forming either liquid or crystallised compounds, frequently having the composition $C^{10}H^{16}.HCl$ or $C^{10}H^{16}.2HCl$; these compounds, called artificial camphors, have the same rotatory power as the oils from which they are produced. Similar compounds are formed with *hydrobromic* and *hydriodic* acid.

Natural camphenes treated with *acids*, especially with *strong sulphuric acid*, generally undergo an alteration of molecular arrangement without change of chemical constitution, the odour being for the most part greatly altered, sometimes also the density and boiling point; but the most characteristic alteration is the loss of optical rotatory power. A camphene often yields several isomeric modifications by treatment with different acids, or by repeated treatment with the same acid. The new camphenes thus produced are called camphenes of the second order, or sometimes campherenes. Another class, called camphenes of the third order, or sometimes camphilenes, are obtained by the action of lime or baryta at high temperatures on the hydrochlorates of other camphenes; these are also optically inactive; and generally differ greatly in odour from the original camphenes, but often exhibit nearly the same specific gravity and boiling point. The camphenes of the second and third orders are decomposed by chlorine, bromine, and iodine, and form liquid or crystallised compounds with hydrochloric, hydrobromic, and hydriodic acids.

The camphenes are a very numerous class of bodies; the principal of them are:

Oil of bergamot
Borneene
Carvene
Caoutchin
Cinæbene
Neutral oil of cloves
Oil of copaiba
Oil of elemi
Gaultherilene
Oil of gomart
Oil of hops
Oil of juniper
Oil of lemon
Oil of orange
Oil of parsley
Oil of pepper
Petrolene
Oil of savin
Thymene
Tolene
Oil of turpentine

For details relating to specific gravity, boiling point, vapour-density, and rotatory power, see the several oils. (Handw. d. Chem. ii. [2] 691; Gm. xiv. 271—322 and 356—404.)

CAMPHERENES. Camphenes of the second order (p. 724).

CAMPHERYL or **CAMPHERILE.** A name applied by Laurent to the impure camphorone (*q. v.*) which he obtained from camphorate of calcium.

CAMPHIC ACID. $C^{10}H^{16}O^2$?—A product obtained, together with borneol, by heating camphor with alcoholic soda-solution in sealed tubes to 170°—190° C.

$$\underset{\text{Camphor.}}{2C^{10}H^{16}O} + H^2O = \underset{\text{Borneol.}}{C^{10}H^{18}O} + \underset{\text{Camphic acid.}}{C^{10}H^{16}O^2}.$$

On neutralising the product with sulphuric acid, dissolving out the camphate of sodium with alcohol, evaporating and again adding sulphuric acid, the camphic acid separates as a nearly solid, coloured mass, heavier than water, sparingly soluble therein, easily soluble in alcohol. It is decomposed by nitric acid. The potassium and sodium-salts are nearly insoluble in strong alkaline leys; they precipitate the salts of copper, iron, lead, silver, and zinc, not those of the alkaline-earth metals; all the precipitates are soluble in a large quantity of water. (Berthelot, Ann. Ch. Phys. [3] lvi. 94.)

CAMPHIDES. This term was applied by Laurent to nuclei in which the combustible hydrogen is replaced by oxygen.

CAMPHILENE. Deville's name for the camphene obtained by treating hydrochlorate of turpentine-oil with lime. Camphenes of the third order (p. 724) are sometimes called camphilenes.

CAMPHIMIDE. See CAMPHORIMIDE.

CAMPHIN. $C^{10}H^{18}$ or C^9H^{16}? (Claus, J. pr. Chem. xxv. 262; Gm. xiv. 448.)—Formed, together with campho-creosote, colophene, and campho-resin, by triturating camphor with an equal weight of iodine, and distilling. A black mass then remains containing campho-resin, and the distillate separates on standing, into a watery layer containing hydriodic acid, and an upper oily layer containing camphin, campho-creosote, and colophene. To obtain the camphin, the mixture is agitated with mercury, to remove iodine, then rectified *per se*, and the most volatile portion shaken up with potash-ley, and repeatedly rectified over potash-lime to remove iodine; it may also be freed from the last traces of iodine by setting it aside with potassium and rectifying.

Camphin is a thin colourless oil of specific gravity 0·827 at 25° C., and boiling at 167—170° under a pressure of 28 inches. It has a pleasant odour, like that of oil of mace, somewhat also like turpentine. It gave by analysis 86·06 per cent. C and 12·79 H; the formula $C^{10}H^{18}$ requires 86·96 C and 13·04 H, while C^9H^{16} requires 87·10 C and 12·90 H. Gerhardt regarded it as impure cymene, $C^{10}H^{14}$ (89·5 C and 10·5 H).

Camphin burns with a bright but very smoky flame. It dissolves in *alcohol*, *ether*, *oil of turpentine*, and *rock-oil;* but not in water, weak alcohol, potash, or dilute acids, or even in strong hydrochloric acid. It absorbs a small quantity of *hydrochloric acid gas*. It is but slightly attacked by *sulphuric acid*. *Nitric acid*, with aid of heat, converts it into a yellow nitrogenised oil, smelling like cinnamon, or by prolonged heating, into a red oil soluble in potash. *Pentachloride of antimony* converts it into a resin.

Camphin is readily decomposed by *chlorine* and *bromine*, yielding *substitution-products*. The chlorocamphins are transparent, colourless, oily bodies, which, when treated with alcoholic potash, yield chloride of potassium and a chlorinated oil having an agreeable odour. Claus obtained two compounds, which he regarded as $C^9H^{13}Cl^3$ and $C^9H^{10}Cl^6$.

CAMPHINE. This term is applied in commerce to purified oil of turpentine, obtained by carefully distilling the oil over quick lime, sometimes also rectifying it over dry chloride of lime; in this manner it is obtained quite free from resin. In some cases, the oil is treated with sulphuric acid previous to rectification. This purified turpentine-oil is much used for burning in lamps, giving a very brilliant light. It is however very apt to smoke, and must therefore be burnt in lamps of peculiar construction, with very strong draught. A solution of camphine in three times its volume of alcohol of specific gravity 0·820, sometimes with addition of a little ether to ensure more complete solution, is also used as an illuminating material, and may be burned in ordinary lamps with argand burners.

CAMPHOCREOSOTE. A product of the decomposition of camphor by iodine at high temperatures; according to Schweizer, it is probably identical with carvacrol (*q. v.*)

CAMPHOGEN. Dumas' name for the hydrocarbon $C^{10}H^{14}$, obtained from camphor by the action of phosphoric anhydride; it is identical with cymene (*q. v.*)

CAMPHOL. This name was applied by Gerhardt to the camphor of the Lauraceæ; but Berthelot has recently applied it (Ann. Ch. Phys. [3] lvi. 78), to Borneol or Borneo-camphor, which he regards as the alcohol of a series in which common camphor is the aldehyde, thus:

Ethyl-series.		Camphyl-series.	
Ethyl-alcohol,	C^2H^6O	Camphol,	$C^{10}H^{18}O$
Aldehyde,	C^2H^4O	Camphor,	$C^{10}H^{16}O$
Acetic acid,	$C^2H^4O^2$	Camphic acid,	$C^{10}H^{16}O^2$
Chloride of ethyl,	C^2H^5Cl	Chloride of camphyl,	$C^{10}H^{17}Cl$
Ethylene,	C^2H^4	Camphene,	$C^{10}H^{16}$

Camphol is produced by treating camphor with alcoholic potash (p. 626), just as benzylic alcohol is produced from benzoic aldehyde (p. 578). It is also formed by distilling amber with ¼ of its weight of potash and a large quantity of water.

From later experiments by Berthelot and Buignet (Compt. rend. l. 606), it appears that the several bodies to which the name camphol has been applied, are isomeric but not identical, being especially distinguished by their different rotatory power, which in camphol from common camphor = +44·9°; in natural camphor or borneol, = +33·4°; in camphol from amber = +4·5°; while in lævo-rotatory borneol, or camphol obtained from madder-camphor (p. 626), it is −33·4°.

According to Berthelot, camphol heated with acids unites with them, like all alcohols, with elimination of water. The resulting compound ethers may be purified by removing the excess of acid with slaked lime and ether, and distilling off the excess of camphol by prolonged heating at 150°C. They are colourless, neutral, soluble in alcohol and ether; some are liquids, others crystalline; the latter melt at a lower temperature than camphol. Alkalis decompose them into acid and camphol, the latter exhibiting its original properties. *Benzoate of camphol*, $C^{17}H^{22}O^2 = C^7H^5(C^{10}H^{17})O^2$, is a neutral, colourless, inodorous oil.—*Stearate of camphol*, $C^{28}H^{52}O^2 = C^{18}H^{35}(C^{10}H^{17})O^2$, is colourless, inodorous, viscid, solidifying after a while in a crystalline mass.—*Chloride of camphyl*, $C^{10}H^{17}Cl$, obtained by heating camphol (borneol) with strong hydrochloric acid to 100° C. in a sealed tube for 8 or 10 hours, and purified by washing with dilute potash and crystallisation from alcohol, has the aspect, odour, and empirical composition of hydrochlorate of turpentine-oil or artificial camphor ($C^{10}H^{16}.HCl$), but turns the plane of polarisation to the left, somewhat less strongly than borneol. Heated to 180° C. with alcoholic soda-solution, it yields chloride of sodium and borneol. By this and by its rotatory power, it is sufficiently distinguished from hydrochlorate of turpentine-oil. (Handw. d. Chem. 2te Aufl. ii. [2] 695.)

CAMPHOLENE. C^9H^{16}. A liquid hydrocarbon obtained by distilling campholic acid with phosphoric anhydride. Vapour-density 4·353. (Delalande.)

CAMPHOLIC ACID. *Bornenic acid.* $C^{10}H^{18}O^2 = C^{10}H^{17}O.H.O.$—Produced by the action of hydrate of potassium on camphor. The quantity found under the ordinary atmospheric pressure is but small: but if the camphor be enclosed, together with potash-lime, in a sealed combustion tube of the ordinary dimensions, and its vapour made to pass several times over the heated potash-lime, about 5 or 6 grammes of purified acid may be obtained from each tube. To isolate the acid, the contents of the tube are digested in water, and the solution decomposed by a stronger acid. The campholic acid is then deposited as a crystalline mass, which may be purified by distillation. It is white, and crystallises well from a mixture of alcohol and ether; melts at 50° C.; boils without alteration towards 250°. Insoluble in water, but imparts to it an aromatic odour. Vapour-density 6·058. Distilled with phosphoric anhydride, it yields campholene, carbonic oxide being probably evolved at the same time:

$$C^{10}H^{18}O^2 = CO + H^2O + C^9H^{16}.$$

It is monobasic. The *calcium-salt*, $C^{10}H^{17}CaO^2$, is a snow-white crystalline powder obtained by pouring chloride of calcium into a nearly boiling solution of the acid in excess of ammonia. By dry distillation, it yields an oily body called *campholone*, $C^{19}H^{34}O$:

$$2C^{10}H^{17}CaO^2 = Ca^2CO^3 + C^{19}H^{34}O.$$

Campholate of silver, obtained by decomposing the neutral ammonium-salt with nitrate of silver, forms curdy flakes. (Delalande, Ann. Ch. Phys. [3] i. 120.)

CAMPHONE. Syn. of CYMENE.

CAMPHOMETHYLIC ACID. Camphorate of methyl and hydrogen. (See CAMPHORIC ACID, p. 733.)

CAMPHOR. $C^{10}H^{16}O$. (Gm. xiv. 358; Gerh. iii. 621).—A crystalline substance obtained from the *Laurus camphora* and other plants in which it exists ready formed. There are three modifications of it, identical in composition and chemical properties, but differing in their action on polarised light, viz. *dextro-camphor*, which turns the plane of polarisation to the right, *lævo-camphor*, which turns it to the left, and *inactive camphor*, which has no action on polarised light.

a. *Dextro-camphor. Laurel* or *common camphor*. This variety exists in the wood and bark of several trees of the Lauraceous order, chiefly in the *Laurus camphora*, a tree indigenous in Japan, Java, Sumatra, and Borneo. The process of extraction is very simple. In China and Japan, the wood, sawn into billets, is distilled with water in a kettle covered with an earthen capital lined with rice-straw, on which the crystals of camphor are deposited, being carried up by the aqueous vapour. The crude camphor thus obtained is exported to Europe, where it is purified by sublimation. In Sumatra and Borneo, the wood is split with wedges, and the camphor, which is found between the fibres in tears and crystals, is extracted; a single tree sometimes yields as much as twenty pounds.

Dextro-camphor is also produced artificially by the action of nitric acid on borneol or camphor of Borneo, $C^{10}H^{18}O$ (pp. 626, 726).

Camphor crystallises by sublimation, or by slow deposition from an alcoholic solution, in octahedrons or segments of octahedrons. It is white and semi-transparent, like ice, rather tough, sectile, and not easily reduced to powder without the aid of a little alcohol. It melts at 175° C. and boils at 204° C. evaporating completely away without alteration. Its specific gravity varies from 0·986 to 0·996. Vapour-density = 5·317 (Dumas). Water dissolves $\frac{1}{1000}$ pt. of camphor, and thereby acquires its peculiar smell and taste. When small bits of camphor are thrown into water in a broad basin, they revolve and move about with more or less velocity, in proportion to their smallness. These rotations are attributed to the force exerted by the vapours rapidly exhaled from the camphor on the surface of the water; but the explanation is not very satisfactory. If a pin-point slightly smeared with oil be dipped into the water, all the motions cease instantly, and the particles of camphor are repelled from the pin-spot by the spreading film of oil. The dispersion of the camphor-vapour is made very striking by the repulsion of the water on a moistened saucer from the points on which bits of this substance are laid.

Laurel-camphor is soluble in alcohol, ether, acetone, acetic acid, wood-spirit, sulphide of carbon, and oils. 100 pts. of alcohol of specific gravity 0·806 dissolve 120 pts. of camphor. It is thrown down almost entirely in flocks by the addition of water. Camphor augments in a remarkable degree the solubility of corrosive sublimate in spirit of wine.

The optical rotatory power of the alcoholic solution of camphor, is 47·4 for a length of 100 millimetres. According to Arndtsen (Ann. Ch. Phys. [2] liv. 403), it increases with the refrangibility of the rays much more quickly than is observed in any other substance. Solid camphor does not exhibit any rotatory power.

Reactions.—1. Camphor, when set on fire in the *air*, burns with a smoky flame, producing water and carbonic acid. Spongy *platinum*, or a coil of fine platinum wire laid on camphor, begins to glow when the camphor is set on fire, and continues glowing after the flame is blown out. Camphor is set on fire by *chlorochromic acid*.—2. By prolonged boiling with *nitric acid* or *permanganate of potassium*, it is converted into camphoric acid (p. 730).—3. Heated with *strong sulphuric acid* to 100° C. for 12—13 hours, it is converted into camphrene, $C^9H^{12}O$, with evolution of sulphurous anhydride and separation of charcoal (Chautard, Compt. rend. xliv. 66). According to Delalande (Instit. 1839, p. 399), camphor heated with excess of strong sulphuric acid, is converted into a volatile oil, which has the chemical properties and composition of common camphor, but less rotatory power, and when heated with potash to nearly 200° C. is converted into a solid camphor, whose rotatory power is intermediate between that of common camphor and that of the oily camphor. Gerhardt supposed that the oil obtained by Delalande was cymene; according to Chautard, it is camphrene containing camphor.—4. Camphor-vapour passed through a *red-hot glass* or *porcelain tube*, yields a combustible gas and an oil soluble in alcohol (Saussure).—5. When the vapour of camphor is passed over *red-hot iron*, an oily liquid is produced, containing naphthalene and a hydrocarbon boiling at 140° C. and having the composition of benzene (D'Arcet, Ann. Ch. Phys. [2] lxvi. 110).—6. Camphor distilled with

2 pts. *alumina* or *clay*, is resolved into carbonic anhydride, carburetted hydrogen, empyreumatic oil, and a residue of charcoal.—7. Distilled with *phosphoric anhydride*, it is resolved into water and cymene, $C^{10}H^{14}$ (Delalande, Ann. Ch. Phys. [3] i. 368). Heated with concentrated phosphoric acid, it volatilises for the most part undecomposed. It is also resolved into water and cymene by distillation with *chloride of zinc*. —8. Camphor-vapour passed over *red-hot lime*, yields camphrone, $C^{30}H^{44}O$, an oily liquid boiling at 75° C. At a very bright red heat, this product is resolved into carbonic oxide, carburetted hydrogen, and naphthalene (Frémy, Ann. Ch. Phys. lix. 16).—9. When the vapour is passed over heated *potash-lime*, under pressure, campholate of potassium, $C^{10}H^{17}KO^2$ is produced (Delalande, p. 726).—10. Camphor heated to 180°—200° C. with *alcoholic potash* or *soda*, is converted into borneol (Berthelot, pp. 626, 726).—11. When camphor is triturated with *iodine*, and the mixture is distilled, a dark-coloured oily liquid passes over, containing camphin, camphocreosote, and colophene, and a blackish residue is left, containing campho-resin (Clauss, p. 725).—12. *Bromine* unites with camphor, forming an instable bromide of camphor, $C^{10}H^{16}O.Br$, which is crystalline, and is decomposed by heat, by contact with air, and by the action of ammonia.—13. *Chlorine* exerts but little action on camphor, even in sunshine.—14. With *pentachloride of phosphorus*, camphor yields oxychloride of phosphorus, and a crystalline substance, $C^{10}H^{16}Cl^2$, having the aspect of artificial camphor (hydrochlorate of turpentine-oil). It remains dissolved in the oxychloride, and may be precipitated by water (Gerhardt):

$$C^{10}H^{16}O + PCl^5 = POCl^3 + C^{10}H^{16}Cl^2.$$

This compound yields by repeated dry distillation, a chlorinated oil consisting of $C^{10}H^{15}Cl$. (Gerhardt.)

According to Pfaundler (Ann. Ch. Pharm. cxv. 29), 1 at. camphor heated to about 110° C. with 1 at. PCl^5, yields hydrochloric acid, oxychloride of phosphorus, and chlorocamphene, $C^{10}H^{15}Cl$, which is a white, soft, crystalline substance, having an odour of camphor. Its index of refraction is 1·49327. It is insoluble in water, but dissolves in 3·5 pts. of 87 per cent. alcohol at 14° C., forming an optically inactive solution. The crystals volatilise rather quickly at ordinary temperatures, melt at about 60° C., and then sublime, decomposing at higher temperatures. With 2 at. pentachloride of phosphorus to 1 at. camphor, chloride of camphene, $C^{10}H^{16}Cl^2$, is obtained in white crystals, resembling the preceding in aspect and in odour, but softer, and having an index of refraction = 1·50553. It dissolves in 4·95 pts. of 87 per cent. alcohol, at 14° C., forming a solution possessing lævo-rotatory power. The crystals volatilise rather quickly at ordinary temperatures, and melt with partial sublimation near 70°. —15. If *chlorine* be passed through the solution of camphor in *trichloride of phosphorus*, various substitution-products are formed, according to the time for which the action of the chlorine is continued. *Tetrachlorocamphor*, $C^{10}H^{12}Cl^4O^2$, has been isolated, though not quite pure. If the action be continued for a long time, and assisted by heat, a colourless product is at length obtained, having the aspect of white wax, and consisting of *sexchloro-camphor*, $C^{10}H^{10}Cl^6O$ (Claus, J. pr. Chem. xxv. 259). —16. When camphor is heated with *mercuric chloride*, hydrochloric acid is evolved, together with an odour of turpentine, and a carbonaceous mass containing calomel remains.—17. *Pentachloride of antimony* attacks camphor strongly, giving off hydrochloric acid, and forming a resinous substance.—18. *Hydrochloric acid gas* is absorbed by camphor in quantities varying according to pressure and temperature, as shown by the following table, which gives the quantity of the gas (HCl) absorbed by 100 pts. camphor, at the temperature *t* and barometric pressure *b*:

t	24°	20°	18·5°	18·5°	13°	9°	7°	7°	3°	3° C.
b	747	740	735	744	320	288	270	740	232	738 mm.
HCl	19·0	20·0	20·4	20·5	15·3	15·8	16·3	240	17·0	26·0

At a certain low pressure, camphor no longer absorbs hydrochloric acid gas. This pressure varies with the temperature, being 220 mm. at 12°; 340 mm. at 15·0; 300 mm, at 20°; and 423 mm. at 24° (Bineau, Ann. Ch. Phys. [3] xxiv. 328).—19. *Sulphurous anhydride* is quickly absorbed by camphor, forming a colourless liquid, which is heavier than water, dissolves iodine and camphor, and when saturated with camphor, contains 4 pts. camphor to 1 pt. SO^2. It gives off sulphurous anhydride even at ordinary temperatures. The quantities absorbed by 100 pts. camphor at various pressures and temperatures, are given in the following tables (Bineau, *loc. cit.*):

t	24°	24°	15·5°	15·5°	12·5°	12·5°	2°	8°	4°	4°	2°	2° C.
b	524	745	355	744	529	727	304	682	490	720	649	650 mm.
SO^2	25·5	35·4	28·0	47·6	37·3	50·5	33·0	57·4	46·0	73·6	48·4	72·0

At 700 mm. pressure, 100 pts. camphor absorb of SO^2:

at	24°	20°	15·5°	14°	12·5°	10°	8°	4° C.
	33·1	37·7	44·3	46·8	48·9	54·0	58·6	70·5

—20. Camphor absorbs the vapour of *peroxide of nitrogen* (or nitric oxide in presence of air), forming a liquid which is decomposed by water, dissolves camphor, and when saturated therewith at 18° C., contains 100 camphor to 26—27 peroxide of nitrogen. (Bineau.)

β. Lævo-camphor.—When the essential oil of feverfew (*Pyrethrum parthenium*) is fractionally distilled, and the portion which distils between 200° and 220° C. is collected apart, it deposits on cooling a large quantity of camphor, similar in all respects to common camphor, excepting in its optical rotatory power, which is equal and opposite, viz. $[\alpha] = -47{\cdot}4$ for a length of 100 millimetres. The camphor treated with nitric acid yields lævo-camphoric acid. (Dessaignes and Chautard, J. Pharm. [3] xiii. 241; Chautard, Compt. rend. xxxvii. 166.)

γ. Inactive Camphor.—According to Proust, the essential oils of several labiate plants, viz. rosemary, marjoram, lavender, and sage, often deposit a substance like camphor. Lavender camphor has the same composition as laurel camphor, but is without action on prolonged light. (Dumas, Ann. Ch. Phys. xiii. 275; Biot, Compt. rend. xv. 710.)

Bodies resembling camphor but of undetermined modification, have been obtained by the action of nitric acid on the essential oils of tansy, semen-contra, valerian, and sage. Lastly, when amber is treated with nitric acid, it yields a distillate containing camphor, which may be extracted by saturating with carbonate of potassium and igniting with ether.

CAMPHOR, ARTIFICIAL. Syn. with HYDROCHLORATE OF TURPENTINE-OIL. (See TURPENTINE.)

CAMPHOR OF BORNEO. See BORNEOL.

CAMPHOR, OIL OF. When the branches of the camphor-tree (*Laurus camphora*) are distilled with water, a volatile oil passes over together with camphor. This oil is mobile, colourless, has a strong odour of camphor and considerable dextrorotatory power, and is resolved by fractional distillation into an oil boiling at 180° C. and a portion boiling at 205°; the latter appears to be essentially the same as common camphor. The oil boiling at 180° is very much like oil of lemon, possesses strong dextro-rotatory power, and forms with hydrochloric acid a crystalline compound, which melts at 42°, and gives by analysis 57·34 per cent. C, 8·6 H, and 33·83 Cl, agreeing with the formula $C^{10}H^{16}.2HCl$. (Lallemand, Ann. Ch. Phys. lvii. 404.)

The wood of *Dryabalanops Camphora*, from which borneol is obtained, likewise yields by boiling with water, a camphor oil, separable by fractional distillation into two volatile oils, having the composition $C^{10}H^{16}$, one boiling between 180° and 190° C., the other at about 260°, and a resin, $C^{30}H^{46}O^2$ (?), which melts at a temperature a little above 100° (Lallemand). It is remarkable that the oil of Dryabalanops examined by Lallemand, did not contain borneol, and that even the most volatile portion of it had a boiling point much higher than that of borneene (p. 626). The subject requires further examination. (See DRYABALANOPS.)

CAMPHORAMIC ACID. $C^{10}H^{17}NO^3 = \left.\begin{matrix} N.H^2.(C^{10}H^{14}O^2)'' \\ H \end{matrix}\right\} O.$ (Laurent, Compt. chim. 1845, p. 147.)—Derived from acid camphorate of ammonium by elimination of 1 at. water:

$$C^{10}H^{15}(NH^4)O^3 - H^2O = C^{10}H^{17}NO^3.$$

The ammonium-salt of this acid is produced by the action of ammonia on a boiling saturated solution of camphoric anhydride ($C^{10}H^{14}O^3 + 2NH^3 = C^{10}H^{16}(NH^4)NO^3$), and on treating the solution of this salt with hydrochloric acid and evaporating, camphoramic acid is deposited in crystals, which may be purified by solution in dilute alcohol and spontaneous evaporation. It is then obtained in splendid crystals, belonging to the trimetric system, $\infty\breve{P}\infty \,.\, \infty\bar{P}\infty \,.\, \breve{P}\infty$, with ∞P and P subordinate. Inclination of the faces: $P\infty : P\infty = 114° 30'$; $\breve{P}\infty : \infty\breve{P}\infty = 122° 45'$; $\breve{P}\infty : P = 155°$; $\infty\breve{P}\infty : \infty P = 131° 40'$. It is colourless, moderately soluble in hot water, less in cold; more easily in alcohol. A small quantity melted on a plate of glass, partly crystallises in rhombs, while the rest solidifies slowly into a transparent vitreous mass.

The acid is monobasic. Its *ammonium-salt*, $C^{10}H^{16}(NH^4)NO^3 + H^2O$, crystallises well, has a slightly acid, bitter, transient taste, and melts at 100° C. It differs from neutral camphorate of ammonium, with which, in the hydrated state, it agrees in composition, by not precipitating the salts of lead, copper, or silver. The *lead-salt*, $C^{10}H^{16}PbNO^3$, is deposited in small crystals, on mixing the concentrated boiling alcoholic solutions of camphoramate of ammonium and acetate of lead, the former in excess, and leaving the liquid to cool. The *silver-salt*, $C^{10}H^{16}AgNO^3$, is obtained as a transparent jelly, composed of minute crystals, on mixing the boiling concentrated solutions of camphoramate of ammonium and nitrate of silver, and leaving the liquid to cool.

CAMPHORANILIC ACID. See Phenyl-Camphoramic Acid.

CAMPHORAMIDE. $C^{10}H^{18}N^2O^2 = N^2.H^4.(C^{10}H^{14}O^2)''$.—When a current of ammonia-gas is passed into the middle of a solution of camphoric anhydride in absolute alcohol, the liquid becomes heated, and yields by evaporation a syrupy mass, insoluble in water, which is probably camphoramide. It is not decomposed in the cold by hydrochloric acid; but when treated with potash, it gives off ammonia, and forms camphorate of potassium. (Laurent, Rev. scient. x. 123.)

CAMPHORESIN. The name given by Claus to the non-volatile product of the action of iodine on camphor (p. 728).

CAMPHORIC ACID. $C^{10}H^{16}O^4 = C^{10}H^{14}O^2.H^2.O^2$. (Gm. xiv. 455; Gerh. iii. 700.)—There are three modifications of this acid, corresponding to those of camphor, viz. *dextro-rotatory*, *lævo-rotatory*, and *inactive*.

Dextro-camphoric or *ordinary Camphoric acid.*—This acid was discovered by Kosegarten (*Diss. de camphora et partibus quæ eam constituant*, Göttingen, 1785), and particularly studied by Laurent (Ann. Ch. Phys. lxiii. 207; Compt. Chim. 1845, p. 141), Malaguti (Ann. Ch. Phys. lxiv. 151), and Liebig (Ann. Ch. Pharm. xxii. 60). To prepare it, common camphor is heated in a retort with ten times its weight of strong nitric acid, the liquid being cohobated several times, and the acid renewed. On evaporating and cooling the residual liquid, the camphoric acid crystallises out, and may be purified by dissolving it in carbonate of potassium, precipitating with nitric acid, and recrystallising several times.

Camphoric acid forms colourless transparent scales or needles, which melt at 70° C., and taste sour and bitter at the same time. It is sparingly soluble in cold water, more readily in boiling water; easily also in alcohol, ether, and fatty oils. According to Brandes, it requires for solution, 88·8 pts. of water at 12·5° C., and 8·6 pts. at 96·25°. Molecular rotatory power of the solution $[\alpha] = + 38{\cdot}875$; this power diminishes considerably on saturating the acid with an alkali.

It gives an abundant precipitate with neutral acetate of lead. By dry distillation it is resolved into water and camphoric anhydride, leaving only a small film of charcoal. It dissolves without alteration in strong nitric and sulphuric acid.

β. *Lævo-camphoric Acid.*—Obtained by the action of nitric acid on the camphor of feverfew (p. 729), has the same composition and chemical properties as dextro-camphoric acid, and rotates the plane of polarisation, by exactly the same amount, to the left. (Chautard, Compt. rend. xxxvii. 166.)

γ. *Inactive Camphoric Acid*, or *Paracamphoric Acid*, is produced by mixing equal weights of dextro- and lævo-camphoric acid. It agrees with ordinary camphoric acid in most of its properties, but has no action on polarised light. (Chautard.)

Camphorates.—Camphoric acid is dibasic, the formula of a neutral camphorate being $C^{10}H^{14}M^2O^4$. The camphorates are odourless, and have a slightly bitter taste. Most of them are sparingly soluble in water. They are decomposed by sulphuric, hydrochloric, and nitric acid.

Camphorates of Ammonium.—The neutral salt, $C^{10}H^{14}(NH^4)^2O^4$, is obtained by passing a current of dry ammonia-gas over camphoric acid, and exposing the product to a current of dry air. It is very soluble in water, and has a slight acid reaction, but no decided taste. An *acid ammonium-salt* is obtained in small prisms, melting above 100° C. by throwing crystals of acid carbonate of ammonium into a boiling solution of camphoric acid. When dried at 100° in a current of air, they lose 19 per cent. of water. They contain, according to Malaguti, 53·57 per cent. carbon, 8·97 hydrogen, and 8·5 nitrogen, whence he deduces the formula $3C^{10}H^{16}O^4.4NH^3 + 9H^2O$, that is to say, a compound of 1 at. neutral camphorate and 2 at. acid camphorate of ammonium; but, according to Gerhardt, the salt is an *acid camphorate*, $C^{10}H^{15}(NH^4)O + 3H^2O$, the formula of which requires 55·3 C, 8·7 H, 6·6 N, and 19·9 per cent. water.

Camphorate of Potassium. $C^{10}H^{14}K^2O^4$.—Crystallises in large nacreous scales when prepared with hydrated camphoric acid, and in small delicate needles when prepared by dissolving camphoric anhydride in potash. According to Bucholz and Bouillon-Lagrange, it is but sparingly soluble in water, whereas Brandes states that it is very deliquescent, and dissolves in a very small quantity of water (probably the sparingly soluble salt was an acid salt). Camphorate of sodium forms limpid, confused, slightly efflorescent crystals, soluble in 200 pts. of cold and 8 pts. of boiling water; also in alcohol.

The *barium-salt* forms laminæ or needles soluble in 600 pts. of boiling water; according to Brandes, in 1·8 pts. water at 19·9° C.

The *strontium-salt* forms colourless laminæ much more soluble than the barium-salt.

Calcium-salt.—The neutral salt forms a non-crystalline mass, neutral to test-paper, nearly insoluble in cold water, soluble in 200 pts. of boiling water, insoluble in alcohol, and containing 7 per cent. water of crystallisation. It falls to powder in contact with the air. By treating carbonate of calcium with camphoric acid, a salt is obtained having an acid reaction, and crystallising in rhomboïdal prisms, containing 37·5 per cent. water, and soluble in 5 pts. of cold water (Bucholz, Brandes). Neutral camphorate of calcium yields, by dry distillation, carbonate of calcium and camphorone:

$$C^{10}H^{14}.Ca^2O^4 = CO^3Ca^2 + C^9H^{14}O.$$

Camphorate of Copper, $C^{10}H^{14}Cu^2O^4$ (at 100°), is obtained by double decomposition as a light green precipitate, nearly insoluble in water. It forms a crystallisable compound with ammonia.

Camphorate of Manganese is very soluble in water. Manganous salts are not precipitated by alkaline camphorates.

Mercurous Camphorate is a white precipitate, nearly insoluble in water.

Camphorate of Silver is a white fusible precipitate, which becomes coloured by exposure to light.

CAMPHORIC ANHYDRIDE. *Anhydrous camphoric acid.* $C^{10}H^{14}O^2.O.$ (Bouillon-Lagrange (1799), Ann. Chim. xxiii. 153.—Laurent, Ann. Ch. Phys. lxiii. 207.—Malaguti, *ibid.* lxiv. 151.)—Obtained by distilling camphoric or ethyl-camphoric acid, and crystallising the product from boiling alcohol. It forms fine prisms without acid reaction, and having no perceptible taste at first, but afterwards irritating to the throat. It dissolves very sparingly in cold water, a little more in boiling water, very abundantly in alcohol, still more in ether. At 130° C. it begins to sublime in beautiful white needles, melts to a colourless liquid at 217°, begins to boil above 270°, and distils without residue. Specific gravity of the crystals 1·194 at 20°·5. They become electric by friction, like resins. Their solution does not precipitate neutral acetate of lead.

Camphoric anhydride boiled with water dissolves very slowly as camphoric acid. The transformation is effected much more quickly by alkalis. It does not absorb dry ammonia gas, but aqueous or alcoholic ammonia converts it into camphoramate of ammonium. Heated with phenlyamine, it yields phenylcamphoramate of phenylammonium and phenylcamphorimide. Heated with strong sulphuric acid, it gives off carbonic oxide, and is converted into sulphocamphoric acid (*q. v.*)

$$\underset{\substack{\text{Camphoric}\\\text{anhydride.}}}{C^{10}H^{14}O^3} + H^2SO^4 = \underset{\substack{\text{Sulpho-}\\\text{camphoric}\\\text{acid.}}}{C^9H^{16}SO^6} + CO$$

CAMPHORIC ETHERS. *Camphorate of Ethyl.* $C^{14}H^{24}O^4 = C^{10}H^{14}(C^2H^5)^2.O^4$.—This body is formed in the dry distillation of ethyl-camphoric acid, and is obtained by pouring water into the alcoholic mother-liquors from which the latter has been precipitated. It is purified by boiling with alkalised water, drying in vacuo, then washing, distilling, and again drying in vacuo. It is an oil having a faint amber colour, a very disagreeable bitter taste, and a powerful odour. Specific gravity 1·029 at 16° C. Begins to boil at 285° or 287°; turns brown a few degrees higher, and leaves a black residue, but the distillate is very pure after being washed. It is perfectly neutral and insoluble in water. Potash decomposes it like other ethers; sulphuric acid dissolves it in the cold without decomposition; at higher temperatures, decomposition takes place, but without blackening or evolution of sulphurous acid. It is not altered by hydrochloric or nitric acid, either cold or hot. (Malaguti, Ann. Ch. Phys. lxiv. 151.)

Tetrachlorinated Camphorate of ethyl, $C^{14}H^{20}Cl^4O^4$, is produced by the action of chlorine on camphorate of ethyl. Neutral; has a bitter persistent taste. Soluble in alcohol and ether. Specific gravity 1·386 at 14° C. When heated it becomes very fluid, and decomposes before boiling. Aqueous potash scarcely attacks it, but alcoholic potash converts it into camphorate, acetate, and chloride of potassium:

$$C^{14}H^{20}Cl^4O^4 + 8KHO = C^{10}H^{14}K^2O^4 + 2C^2H^3KO^2 + 4KCl + 4H^2O.$$

(Malaguti, Ann. Ch. Phys. lxx. 360.)

Camphorate of Ethyl and Hydrogen. Ethyl-camphoric or *Camphovinic acid.* $C^{12}H^{20}O^4 = C^{10}H^{14}(C^2H^5.H)O^4$.—When a mixture of 2 pts. camphoric acid, 4 pts. absolute alcohol, and 1 pt. sulphuric acid is boiled and cohobated several times, a residue is obtained, which, when diluted with water, yields an oily deposit of ethyl-camphoric acid. This acid has, at ordinary temperatures, the consistence of treacle. It is transparent and colourless, has a peculiar odour and a very agreeable taste, not acid, but bitter. It dissolves very sparingly in alcohol and ether. Specific gravity 1·095 at 20·5° C; reddens litmus paper after a while only; dissolves in alkaline solutions, but is decomposed when boiled with them. Water effects the same decomposition after long contact or continued ebullition. By dry distillation it yields water, camphoric anhydride, and camphorate of ethyl, together with very small quantities of alcohol and carburetted hydrogen gas, resulting from secondary decomposition:

$$\underset{\substack{\text{Ethyl-camphoric}\\\text{acid.}}}{2C^{12}H^{20}O^4} = H^2O + \underset{\substack{\text{Camphoric}\\\text{anhydride.}}}{C^{10}H^{14}O^3} + \underset{\substack{\text{Camphoric}\\\text{ether.}}}{C^{14}H^{24}O^4}$$

The alcoholic solution gives a copious precipitate with neutral acetate of lead. (Malaguti.)

Ethyl-camphoric acid is monobasic, the formula of its salts being $C^{10}H^{14}(C^2H^5.M)O^4$. The *ammonium*, *potassium*, *sodium*, *barium*, *strontium*, *calcium*, and *magnesium*-salts are soluble in water. The *zinc*, *copper*, *lead*, *mercury*, and *silver*-salts are insoluble or sparingly soluble. The copper-salt, obtained by precipitating sulphate of copper with ethyl-camphorate of ammonia, is probably a sesquibasic salt. (Malaguti, Ann. Ch. Phys. lxiv. 151.)

Camphorate of Methyl and Hydrogen. Methyl-camphoric or *Camphomethylic acid.* $C^{11}H^{18}O^4 = C^{10}H^{14}(CH^3.H)O^4$.—Obtained in the same manner as ethyl-camphoric acid, substituting wood-spirit for alcohol. The residue of the third distillation yields, when washed with water and left at rest, a crystalline mass, which is to be pressed between paper and boiled with water. It then forms an acid liquid, at the bottom of which some drops of oil collect, changing after a few days into well-defined, colourless, shining crystals of methyl-camphoric acid. These crystals are either needles arranged in radiating groups, or small four-sided or six-sided laminæ; but on dissolving them in ether and leaving the solution to evaporate very slowly, well formed prisms are obtained belonging to the trimetric system, and exhibiting the combination, $P \,.\, \infty P \,.\, \infty \breve{P} \infty$. Inclination of the faces, $\infty P : \infty P = 106° 30'$; $\infty \breve{P} \infty : \infty P = 126° 45'$; $\infty P \infty : P = 115° 25'$ and $66° 4'$; $P : P = 160° 30'$. The four-sided laminæ are hemihedral, and exhibit only the combination $\frac{P}{2} \,.\, 8\breve{P}\infty$, with cleavage perpendicular to $\infty \breve{P} \infty$.

Methylcamphoric acid is very little soluble in water, very soluble in alcohol, ether, and chloroform. The solutions are strongly acid, and turn the plane of polarisation of a ray of light to the right: $[\alpha] = +51° 4'$. The acid melts at about 68° C., and remains viscid a long time after cooling. By distillation it yields camphoric anhydride, a viscid liquid, and a slight residue of carbon. Boiled with caustic potash, it gives off wood-spirit and is converted into camphorate of potassium.

The aqueous and alcoholic solutions of the acid form a white crystalline precipitate with acetate of lead, soluble in excess of the acetate; with acetate of copper, a greenish crystalline precipitate; with baryta-water, they form a cloud, which disappears on adding a drop of nitric acid. They have no action on lime-water or on soluble barium-salts, but form a slight cloud with nitrate of silver. Oxide of silver is reduced by them, producing a blackish deposit. (Low, Ann. Ch. Phys. xxxviii. 483.)

CAMPHORIMIDE. $C^{10}H^{15}NO^2 = N.H.(C^{10}H^{14}O^2)''$.—Obtained by heating neutral camphoramate of ammonium to 150° or 160° C., or by melting or distilling camphoramic acid:

$$\underset{\substack{\text{Camphoramic}\\\text{acid.}}}{C^{10}H^{17}NO^3} = \underset{\text{Camphorimide.}}{C^{10}H^{15}NO^2} + H^2O$$

and:

$$\underset{\substack{\text{Camphoramate of}\\\text{ammonium.}}}{C^{10}H^{16}(NH^4)NO^3} = \underset{\text{Camphorimide.}}{C^{10}H^{15}NO^2} + NH^3 + H^2O.$$

It is purified by solution in boiling alcohol and crystallises on cooling. It is colourless, volatilises at a high temperature without decomposition, and dissolves easily in boiling alcohol, crystallising, on cooling, in tufts like fern leaves, beautifully divided; or by very slow cooling in hexagonal tables, oblique and much elongated. From a solution in weak alcohol, it is gradually deposited in the form of a gummy, transparent substance, which solidifies after some hours in opaque tubercles. The alcoholic solution gives off ammonia when boiled with potash. It dissolves at a gentle heat in strong sulphuric acid, and, on pouring a few drops of water into the solution, a white crystalline deposit is formed. (Laurent, Compt. chim. 1845, p. 147.)

CAMPHORIN. *Camphorate of Glyceryl.*—Produced by heating camphoric acid with glycerin. Viscid; soluble in ether; decomposed by oxide of lead, yielding glycerin and camphorate of lead. (Berthelot.)

CAMPHORONE. *Phorone* (Gerhardt); *Camphoryl* (Laurent). $C^9H^{14}O$. — This compound, the acetone of camphoric acid, was first obtained in an impure state, as a product of the decomposition of that acid, by Laurent (Ann. Ch. Phys. [2] lxv. 329), afterwards prepared pure and more thoroughly examined by Gerhardt and Liès-Bodart (Compt. chim. 1849, p. 385).

Camphorone is produced, like other acetones, by the dry distillation of the calcium-salt of the acid:

$$\underset{\text{Camphorate of calcium.}}{C^{10}H^{14}O.Ca^2.O^2} = \underset{\text{Carbonate of calcium.}}{CO.Ca^2.O^2} + \underset{\text{Camphorone.}}{C^9H^{14}O}$$

It is best to operate only on small quantities at a time. The brown or yellow oil which passes over is purified by fractional distillation, a small quantity of tar remaining behind.

Camphorone is likewise obtained, together with other products, by distilling with lime either of the following substances: 1. *Acetic acetone*, which differs from it only by the elements of water ($3C^3H^6O - 2H^2O = C^9H^{14}O$). On rectifying the distillate, oxide of mesityl, $C^6H^{10}O$, passes over at about 131° C., and camphorone between 200° and 205° (Fittig, Ann. Ch. Pharm. cx. 33).—2. *Grape-sugar.* The distillate yields on rectification, an oil boiling at 86° C., having the composition of metacetone, $C^{18}H^{30}O^3$ (and converted into camphorone, or a body isomeric with it, by distillation with phosphoric anhydride), while camphorone passes over at 208° (Liès-Bodart, Compt. rend. xliii. 394).—3. The juice of *ripe mountain-ash berries*, which contains a small quantity of malic acid: this method, however, does not always yield it. (Liès-Bodart, *loc. cit.*)

Camphorone is a colourless or yellowish oil, very mobile, lighter than water: and having a strong odour like that of peppermint. It boils at 208° C. (Gerhardt), and volatilises undecomposed, yielding a vapour whose density = 4·982 (Gerhardt and Liès-Bodart), by calculation for 2 vol. = 4·784. It is insoluble in water, but dissolves in alcohol and very readily in ether. It does not unite either with acids or with alkalis, and according to Limpricht (Ann. Ch. Pharm. xciv. 246), differs from other acetones in not combining with acid-sulphites of alkali-metals.

Camphorone becomes darker in colour when exposed to the air. It dissolves with blood-red colour, in strong sulphuric acid, and is for the most part precipitated therefrom by water. It is resinised by nitric acid. Phosphoric anhydride acts quickly upon it at a high temperature, converting it, by abstraction of water, into cumene, C^9H^{12} (not mesitylene), which passes over in fractional distillation at 170° C., a carbonaceous mass being left behind. Pentachloride of phosphorus converts it into a chlorinated oil, $C^9H^{13}Cl$, boiling at 175° C., lighter than water, insoluble therein, easily soluble in alcohol. The alcoholic solution, saturated with ammonia-gas, yielded a crystalline substance, probably $C^9H^{15}N.HCl$ (Liès-Bodart). Camphorone heated with *potassium*, gives off hydrogen, and appears to form the compound $C^9H^{13}KO$ (Liès-Bodart). With *potash-lime* it becomes heated, and appears to enter into combination; the mixture heated to 240° C. gives off a colourless oil, apparently different from camphorone, while a resinous substance remains with the alkali. (Gerhardt and Liès-Bodart.)

CAMPHORYL. $C^{10}H^{14}O^2$. The diatomic radicle of camphoric acid, &c. The same term was applied by Laurent to camphorone.

CAMPHOSULPHURIC ACID. See Sulphocamphoric Acid.

CAMPHOVINIC ACID. Camphorate of Ethyl and Hydrogen. (See Camphoric Ethers, p. 732.)

CAMPHRENE. A product of the decompsition of camphor by sulphuric acid (p. 728).

CAMPHRONE. $C^{30}H^{44}O$.—A liquid produced by passing camphor over red-hot lime. It is a light oil, having a strong and peculiar odour, quite different from that of camphor. It boils at 75° C., is insoluble in water, soluble in alcohol and in ether. It is produced from camphor by abstraction of water ($3C^{10}H^{16}O - 2H^2O = C^{30}H^{44}O$), and is perhaps identical with the product obtained by heating camphor with clay, or by passing the vapour of camphor through a red-hot porcelain tube. (Frémy, Ann. Ch. Phys. [2] lix. 16.)

CAMWOOD. See Barwood (p. 517).

CANAANITE. A greyish scapolite rock, from Canaan, Connecticut, containing 53·37 per cent. SiO^2, 4·10 Fe^4O^3, 10·38 Al^4O^3, 25·80 Ca^2O, 1·62 Mg^2O, and 4·00 CO^2. (Dana, ii. 203.)

CANADA BALSAM. See Balsams (p. 492).

CANCERIN. An artificial guano from Newfoundland.

CANCHA-LAGUA. See CACHA-LAGUA (p. 701).

CANCRINITE. A massive mineral found near Miask in the Ural, in the Mariinskaja mine in the Tunskinsk mountains, Siberia, and in Litchfield in the State of Maine. It cleaves parallel to the faces of a hexagonal prism, has an uneven fracture, light rose-red colour and waxy lustre, nacreous on the cleavage faces; transparent or strongly translucent. Specific gravity 2·45 to 2·46. Hardness 5·0—5·5. It melts to a white tumefied glass. Hydrochloric acid dissolves it readily, with efflorescence and separation of gelatinous silica.

The following are analyses of cancrinite: 1. From Miask; light red: *a.* Specific gravity 2·453 (G. Rose, Pogg. Ann. xlvii. 375); *b.* Specific gravity 2·489 (Pusirewsky, Kokscharow's *Materialen zur Mineralogie Russlands*, i. 81).—2. From the Tunskinsk Mountains, yellow; *a.* Specific gravity 2·449 (Struve, Pogg. Ann. xc. 613); *b.* Specific gravity 2·448 (Pusirewsky).—3. From Litchfield. *a.* Yellow. Specific gravity 2·448; *b.* Greenish. Specific gravity 2·461. (Whitney, *ibid.* lxx. 431.)

	From Miask.			From the Tunskinsk Mts.		From Maine.	
	G. Rose.		Pusirewsky.	Struve.	Pusirewsky.	Whitney.	Whitney.
Silica	6·38		5·55	8·51*	5·61	5·95	5·92
Carbonic anhydride	40·43		35·96	38·33	37·72	37·72	37·20
Alumina	28·227		29·57	28·55	27·27	27·55	27·59
Ferric and Manganic oxides	—		0·19	—	—	0·75	0·27
Lime	6·70		5·68	4·24	3·11	3·67	5·26
Soda	17·52		18·53	20·37	21·60	20·27	20·46
Potash	0·70		—	—	—	0·67	0·50
Water	—		3·69	—	4·07	2·62	3·28
		SO^3	0·32				
	100·00		99·49	100·00	99·86	99·60	100·48

From these results, Rammelsberg concludes that the mineral is a mixture of carbonate of calcium with elæolite, containing a smaller proportion of potash and more water than the usual amount. (Rammelsberg's *Mineralchemie*, p. 653; Dana, ii. 232.)

CANDITE. See SPINEL.

CANELLA ALBA. *Costus dulcis. White Cinnamon.*—These names are applied to the bass or inner bark of *Canella alba*, a canellaceous tree growing in the West Indies, especially in Jamaica. It forms reddish-yellow tubes, three feet long and an inch thick, having a pleasant aromatic taste and odour: it contains about 8 per cent. of manna (formerly mistaken for a peculiar kind of sugar called *canellin*), besides starch and the other usual constituents of vegetable structures. By distillation with water, it yields two volatile oils, one lighter than water, the other heavier. If these oils be left in contact with potash-ley, the liquid then diluted with water and distilled, the first portion of the distillate is again lighter than water, and at last a heavy oil is obtained, of very peculiar odour. The potash-ley from which the oils have been distilled, yields by neutralisation with acid and distillation, a heavy oil, smelling like oil of cloves. The light oil of white cinnamon smells very much like oil of cajeput. It may be separated by fractional distillation into several oils, differing greatly in boiling point. White cinnamon contains about 6 per cent. of ash, consisting mainly of carbonate of calcium. (Handw. d. Chem. ii. [2] 927.)

CANNAMINE. Syn. of BRUCINE.

CANNABIN. A poisonous resin extracted from hemp, by exhausting the bruised plant (*Gunjah*) with alcohol, after the greater part of the brown colouring matter has been removed by digestion, first in tepid water, afterwards in solution of carbonate of sodium, then precipitating the chlorophyll with lime, decolorising with animal charcoal, and evaporating. (T. and H. Smith, Pharm. J. Trans. vi. 127, 171.)

From the *Extract. hb. canab. ind. spirituos.* G. Martius has prepared a resin, by treating it with cold alcohol of 83 per cent., mixing the dark green filtrate with water till turbidity ensues, agitating with animal charcoal, filtering and distilling off the alcohol: the resin then separates. It is a light brown, shining substance, becoming glutinous and ductile, has a peculiar narcotic odour, like that of the extract, and an intensely bitter taste. It melts at 68° C., burns with a bright smoky flame, is insoluble in potash and ammonia, but dissolves in alcohol and ether, sparingly also in acids. Volatile oils dissolve it in the cold; fixed oils, with aid of heat.

The narcotic effects of haschish (*q. v.*) are due to hemp-resin. (Handw. d. Chem. ii. [2] 727.)

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* Carbonic anhydride and water.

CANNABIS INDICA. *Indian Hemp.*—This plant, which is indigenous in India and Asia Minor, is much used in the East as an intoxicating agent; the narcotic action appears to reside essentially in a resinous exudation (see Cannabin and Haschish). According to Martius (Chem. Centr. 1856, 225), the herb contains a small quantity of essential oil. The herb dried at 100° C. yielded 18·1 per cent. ash, which, after deduction of carbonic anhydride and sand, contained in 100 pts.: 13·6 potash, 1·4 soda, 32·0 lime, 10·4 magnesia, 8·8 phosphate of iron, 10·1 phosphoric anhydride, 0·3 sulphuric anhydride, 1·2 chlorine, and 22·1 silica.

CANNABIS SATIVA. *Common hemp.*—The leaves of this plant contain 40·5 per cent. carbon, 5·9 hydrogen, 1·8 nitrogen, and 22·0 ash; the stems: 39·9 per cent. C, 5·0 H, 1·7 N, and 4·5 ash. (Kane, J. pr. Chem. xxxii. 354.)

Reich (Jahresber. d. Chem. 1850, Tafel C. p. 661), found in the hemp-plant 4·6 per cent. ash; in the seed 6·3 per cent. The analyses of the ash of the entire plant and of the seed, are given in the following table:

	K^2O	Na^2O	Ca^2O	Mg^2O	Al^4O^3	Fe^4O^3	SO^3	SiO^2	P^2O^5	Cl	CO^2
Plant (Kane)	7·5	0·7	42·0	4·9	0·4	—	1·0	6·7	3·2	1·5	31·9
„ (Reich)	15·8	3·4	35·5	7·7	—	1·1	2·7	7·7	14·2	3·4	8·4
Seed (Reich)	18·5	0·8	20·2	10·2	—	1·2	0·2	9·6	37·6	0·1	1·3

According to Leuchtweiss (Ann. Ch. Pharm. l. 416), hempseed yields 5·6 per cent. ash, containing 20·8 K^2O, 0·6 Na^2O, 25·6 Ca^2O, 1·0 Mg^2O, 33·5 P^2O^5, 13·5 SiO^2, 6·2 sand and charcoal, and small quantities of sulphuric acid, chloride of sodium, and ferric oxide.

Hempseed yields 31·8 per cent. oil, 22·6 albumin, and 6·37 ash, of which 2·47 consists of phosphates (Anderson, Highland Agr. Soc. Journal [new series] No. 50). The oil is $C^{11}H^{22}O^2$, and yields with chlorine and bromine, the substitution-products $C^{11}H^{20}Cl^2O^2$, and $C^{11}H^{20}Br\,O^2$. (Lefort, Compt. rend. xxxv. 134.)

The leaves, flowers, and pollen of hemp have been examined by Schlesinger, (Rep. Pharm. lxxi. 190). The ash of the leaves contains 8·0 per cent. soluble, and 9·2 per cent. insoluble salts. (Kane.)

CANNEL COAL. See Coal.

CANNON METAL. See Copper, Alloys of.

CANTHARIDES. *Spanish Flies* (*Lytta vesicatoria.*)—These coleopterous insects, so well known for their vesicating properties, are much used in medicine in the form of tincture, plasters, &c. Their vesicating power is due to a peculiar acrid principle called cantharidin. Taken internally, they act as a powerful aphrodisiac, and may even destroy life. According to Thoury (J. Pharm. Jan. 1858, p. 65), their poisonous effects may be counteracted by the administration of animal charcoal.

When the aqueous extract of cantharides is treated with alcohol, cantharidin is dissolved, together with other substances, and a brown nitrogenous substance remains. On evaporating the alcoholic extract and treating the residue with ether, the cantharidin dissolves, together with a yellow substance, and an extractive matter remains, which reddens litmus and contains lactic acid, together with a nitrogenous substance. The aqueous decoction of cantharides reddens litmus strongly, and gives with ammonia a precipitate of ammonio-magnesian phosphate (Robiquet, Ann. Ch. lxxvi. 302). When the insects, after being exhausted with boiling water, are treated with boiling alcohol, a greenish fatty oil dissolves, destitute of vesicating power, and consisting, according to Gössmann (Ann. Ch. Pharm. lxxxvi. 317), of olein, stearin, and palmitin.

CANTHARIDIN. $C^5H^{12}O^2$. Isomeric with picrotoxin. (Robiquet, *loc. cit.*; Regnault, Ann. Ch. Phys. [2] lxviii. 151; Thierry, J. Pharm. xxi. 44; Warner, Amer. J. Pharm. xxviii. 193; Procter, Pharm. J. Trans. xxi. 44.)—This substance, which is the active principle of the Spanish fly, is likewise found in the following coleopterous insects:—*Lytta vittata*, *L. ruficollis*, *L. gigas*; *Mylabris cichorii* (Chinese cantharides), *M. pustulata*, *M. punctum*, *M. Sidæ*, *M. Schoenherri*; *Meloe violaceus*, *M. autumnalis*, *M. Furca*, *M. punctatus*, *M. variegatus*, *M. scabrosus*, *M. majalis*. According to Warner, *Lytta vesicatoria*, *L. vittata*, and *Mylabris cichorii* contain about 0·4 per cent. of cantharidin. According to Ferrer, *Mylabris punctatus* contains 0·33 per cent., *M. punctum* 0·19, *M. cichorii* 0·10, *M. Sidæ* 0·12, *M. Schoenherrii* 0·15 per cent.

Cantharidin is prepared from Spanish flies, or better from *Mylabris cichorii*, inasmuch as this insect contains less fat, by digesting the pulverised insects for some days with ether, ether-alcohol, or alcohol alone; completing the extraction in a displacement apparatus, the ether or alcohol being ultimately displaced by water; and distilling off the ether or alcohol. The cantharidin, which crystallises out on cooling, is redissolved and purified with animal charcoal. Ether is preferable to alcohol for the preparation, since it dissolves less of a green oil, which adheres obstinately to the cantharidin (Thierry). According to Procter, cantharidin is best extracted by chloroform. The pulverised cantharides are left in contact for some time with twice their weight of chloroform in a displacement apparatus; the chloroform is then drained off, and finally displaced by alcohol, and the solution is left to evaporate, whereupon the cantharidin crystallises out, saturated with the green oil. It is laid on bibulous paper, which absorbs the greater part of the oil, then crystallised from chloroform mixed with alcohol.

Pure cantharidin forms colourless right-angled four-sided prisms of the dimetric system, acuminated with four faces resting on the lateral faces. According to Procter, it crystallises from ether in oblique four-sided prisms, with dihedral summits, having the aspect of micaceous laminæ. It melts at 200° C., and volatilises in white fumes, which strongly irritate the eyes, nose, and throat, and condense in rectangular prisms, having a strong lustre, and sometimes iridescent.

Cantharidin *per se* is insoluble in *water*, but it is rendered soluble by the presence of other substances (see the last article). It volatilises in small quantity at 104° C., and more quickly at 182°; not with vapour of water. It dissolves readily in *alcohol*, in 34 pts. of cold *ether*, and rather less of hot ether; *acetic ether*, *wood-spirit*, and *acetone* also dissolve it readily when hot, and deposit it on cooling. But its best solvent is *chloroform*, which extracts it even from the aqueous infusion of cantharides. It likewise dissolves in *oils*, both fixed and volatile. Its solution in any of the liquids abovementioned possesses the vesicating power, which, however, is not exhibited by cantharidin in the solid state. A grain of cantharidin mixed with an ounce of lard produces very strong vesication. Cantharidin dissolves in *sulphuric acid*, and is reprecipitated by water; also in hot *hydrochloric* and *nitric acids*, whence it crystallises on cooling; *phosphoric*, *acetic*, and *formic acids* dissolve but little of it at ordinary temperatures. It dissolves in *potash-ley*, and is precipitated by acetic acid. *Ammonia* has no action upon it.

CANTONITE. A variety of sulphide of copper, Cu^2S, from the Canton mine in Georgia, having hexahedral cleavage, bluish-black colour, and semi-metallic lustre. Specific gravity = 4·18. Hardness = 2·0 (N. A. Pratt, Sill. Am. J. [2] xxiii. 409). Genth (*ibid.* 417) regards it as a pseudomorph of covellin after galena.

CANTON'S PHOSPHORUS. A phosphorescent substance prepared by calcining for an hour, at a red heat in a crucible, a mixture of 3 pts. of finely ground oyster-shells with 1 pt. of flowers of sulphur. A better phosphorescence is obtained by calcining the entire shell in a closed crucible, after dusting it over with sulphur. Exposure to bright light is necessary to its luminosity in the dark. The magnesia in the shells is said to be essential to the effect. Gypsum mixed with flour becomes phosphorescent when calcined.

CAOUTCHENE. A hydrocarbon, isomeric with tetrylene, C^4H^8, said by Bouchardat (J. Pharm. Sept. 1837, p. 454), to be produced, together with others, by the dry distillation of caoutchouc (*q. v.*) It has a density of 0·65, boils at 14·5° C., and solidifies in brilliant needles at −10°.

CAOUTCHIN. $C^{10}H^{16}$. (Himly, Ann. Ch. Pharm. xxvii. 41; Gr. Williams, Proceedings of the Royal Society, x. 517; Gm. xiv. 326.)—A hydrocarbon contained, together with many other substances, in the oils produced by distillation of caoutchouc and gutta percha. To separate it, rectified oil of caoutchouc boiling between 140° and 280° C., is repeatedly shaken up with dilute sulphuric acid, then washed alternately with water and potash-ley, and distilled with water several times. The distillate is dehydrated with chloride of calcium and rectified *per se*, the portion which distils between 160° and 175°, being collected apart; from this, by repeated rectification and removal of the portions which pass over below 166° and above 174°, caoutchin is at length obtained, boiling between 168° and 171°; and this product, by repeated fractional distillation, may be brought to boil at 171°. The purification may also be effected by passing dry hydrochloric acid gas into the cooled oil, previously dried over chloride of calcium, whereby hydrochlorate of caoutchin is produced; decanting this liquid from the resin, after it has stood for some days; dissolving it in absolute alcohol; precipitating with water; dehydrating it, and decomposing it by distillation over caustic lime or baryta, and finally over potassium. The product thus obtained is pure caoutchin. (Himly.)

Caoutchin is a transparent, colourless, mobile liquid, having an odour like that of oil of orange, but not quite so agreeable, and a peculiar aromatic taste. It makes transient grease spots on paper. Specific gravity 0·8423 at 0° C. Boils at 175·5° at 0·75 met. pressure. Does not solidify at −39°. Vapour-density 4·461 (Himly), 4·65 (Williams), by calculation (2 vols.) = 4·714. It has but little electric conducting power.

Caoutchin dissolves in 2000 pts. of *water*. It likewise takes up a small quantity of water in the cold, and at higher temperatures a larger quantity, which separates on cooling. It dissolves in all proportions of *alcohol*, *ether*, and *acetate of ethyl;* water separates it from the alcoholic, but not from the ethereal solution, unless alcohol be afterwards added. The alcoholic solution burns with a bright flame, which does not smoke if the caoutchin and alcohol have been mixed in the right proportion. It dissolves slightly in concentrated *acetic* and *formic* acids; also in *oils* both fixed and volatile.

Caoutchin absorbs *oxygen* from the air (45 vols. in fourteen days), and is converted into a resin, part of it, however, volatilising. It is likewise resinised by various *oxidising agents*, *e. g.* by *peroxide of hydrogen*, *nitric oxide*, *nitrous acid*, *strong nitric acid*, and *crystallised chromic acid;* it reduces *cupric oxide* to cuprous oxide and *permanganate of potassium* to peroxide of manganese, but exerts no deoxidising action, even at the boiling heat, on the oxides of lead, mercuric oxide, or chromate of potassium. It is likewise unaffected by sodium, potash, baryta, or lime. With *potassium* it evolves a few gas-bubbles, and covers the metal with a grey film, then remains unaltered.

Of *hydrogen*, caoutchin absorbs 2 vols. in three weeks at 20° C.; of *carbonic anhydride* 11 vols.; carbonic oxide, marsh-gas, and olefiant-gas are not absorbed by it. Of *nitrogen*, it absorbs 5 vols. in five weeks; of *nitrous oxide* a small quantity; *nitric oxide* colours it yellow after a while. It absorbs 3 vols. *ammonia-gas*, but does not mix with aqueous ammonia. It does not absorb cyanogen gas, but *hydrocyanic acid* and *chloride of cyanogen* are absorbed by it in any quantity. It dissolves *phosphorus* and *sulphur* sparingly in the cold, rather more freely when heated; does not absorb sulphydric acid gas, but mixes in all proportions with *sulphide of carbon* and *xanthic acid*. It absorbs *hydrochloric*, *hydrobromic*, and *hydriodic acid gases*, forming the compounds $C^{10}H^{16}.HCl$, &c. It easily dissolves the *chlorides of sulphur*, *phosphorus*, and *carbon*, small quantities of *iodide of sulphur*, and *iodide of phosphorus*. It dissolves a large quantity of *benzoic*, and a small quantity of *oxalic acid;* but not malic, citric, tartrate, tannic, mucic, or succinic acid.

Caoutchin dropped into strong *sulphuric acid*, becomes heated, eliminates sulphurous anhydride, and forms a brown unctuous acid, $C^{10}H^{16}SO^3$, which forms soluble barium and calcium-salts, the latter having, according to Williams, the formula $C^{10}H^{15}CaSO^3$. Boiled with strong *selenic acid*, it turns brown and gradually decomposes. It is not decomposed by *phosphoric* or *phosphorous acid*.

With *chlorine*, caoutchin gives off hydrochloric acid and forms chlorocaoutchin, which, after washing with soda-ley, then with water, and dehydration over chloride of calcium, forms a transparent, colourless, neutral, viscid liquid, of specific gravity 1·433, having a strong ethereal odour and extremely sharp burning taste. It dissolves sparingly in water, easily in alcohol and ether, gives off irritating vapours of hydrochloric acid when distilled *per se*, and yields a variety of oily products by distillation with alkalis.

With *bromine*, caoutchin gives off hydrobromic acid, but remains colourless and transparent; it easily separates bromine from its solution in water, alcohol, or ether, forming heavy drops of oil. Caoutchin mixed with ½ vol. water decolorises bromine till 231·7 pts. bromine have been added to 100 pts. caoutchin, which is in the ratio of 4 at. bromine to 1 at. caoutchin.

By the alternate action of *bromine* and *sodium* on caoutchin, 2 at. hydrogen are removed, and cymene, $C^{10}H^{14}$, is produced. (Williams.)

With *iodine*, caoutchin turns black, and gives off hydriodic acid. It abstracts iodine from solution in water, alcohol, or ether, forming iodocaoutchin, which is a black-brown oil, giving off hydriodic acid when distilled, easily decomposed by heating with oil of vitriol, bromine, chlorine, fuming nitric acid, or potash, nearly insoluble in water, but soluble in alcohol or ether. Caoutchin distilled with excess of iodine, forms a colourless fragrant oil.

Hydrochlorate of Caoutchin, $C^{10}H^{16}.HCl$.—This compound is prepared by passing dry chlorine gas into caoutchin cooled with ice, the delivery-tube terminating a little above the surface of the liquid,—washing the product first with soda-ley, then with water, and drying over chloride of calcium. It is also produced, though in an impure state, by treating caoutchin with trichloride of antimony or mercuric chloride. It is a transparent, colourless, neutral, viscid liquid, having a strong ethereal odour and a very sharp burning taste. Specific gravity 1·433. It gives off very irritating vapours of hydrochloric acid when distilled; is decomposed by boiling with sulphuric acid, with elimination of hydrochloric acid; and yields a variety of oily products by distillation with potash, lime, or baryta. It dissolves sparingly in water, easily in alcohol and ether; also in hot nitric acid and sulphuric acid, separating out unchanged on cooling; but by long boiling with the latter, it becomes carbonised and gives off hydrochloric acid.

CAOUTCHOUC. *Gum elastic*, or *India Rubber*. *Gomme élastique*. *Federharz.*—A product of several genera of arboraceous plants, in which it occurs in the form of a milky sap, and exudes from incisions made in their trunks. Among these trees are the *Siphonia elastica*, *S. Cahuchu*, *Hevea caoutchouc*, *H. Guianensis*, *Jatropha elastica*, *Ficus elastica*, *F. indica*, *F. religiosa*. Formerly the greater part of the good caoutchouc was imported from Para in South America, but an excellent article has of late years been brought from Assam and other districts of India, in which the trees that yield it greatly abound. The juice drawn from the old trees and in the cold season is preferable to that from the young trees and in the hot season, the quantity being greater the higher the incision is made across and through the bark of the tree. The fluid is of a creamy consistence and colour. Its specific gravity, as imported into this country in well-closed vessels, used to vary from 1·0175 to 1·04125 (Ure); the lighter juice yielded 37 per cent. of solid caoutchouc; the denser only 20, though it was the thicker of the two. Some samples of juice have a brownish tinge, which proceeds from a little aloetic matter secreted along with it, which, if dried up in it, gives the caoutchouc a certain degree of viscidity, and by its decomposition eventually destroys its firm texture. Such juice ought to be mixed with its own bulk of water and boiled, whereby the aloes are separated and the caoutchouc concretes into a white elastic mass, free from offensive smell.

Much of the caoutchouc is imported in coarse rough masses. These are cleaned by washing in a trough, with a stream of water, and afterwards kneaded together by the strong pressure of iron-arms in an iron box. The masses thus obtained are next moulded into the forms of square or round cheeses in a press, and finally sliced by knives driven by machinery into thin cakes or ribbands. U.

Faraday recommends for the purification of caoutchouc, to dilute the natural juice with four times its weight of water, and leave it at rest for twenty-four hours. The caoutchouc then separates and rises to the surface in the form of a cream. This is removed, diffused through a fresh quantity of water, and again left to settle at the surface. By repeating this operation till the wash-water is perfectly limpid, the caoutchouc may be obtained very nearly pure. It is then to be spread upon a plate of unglazed earthenware to absorb the water, and afterwards pressed.

Pure caoutchouc is colourless and transparent, but the best found in commerce has a more or less dingy colour from having been dried from the juice in a smoky atmosphere. It is a bad conductor of heat, and a non-conductor of electricity. It is very combustible, and burns without residue, emitting a white light. At ordinary temperatures, it is soft, flexible, and highly elastic. Freshly cut surfaces adhere easily and firmly when pressed together, a property which is made available in forming tubes and vessels out of sheet-caoutchouc. Below 0° C. it becomes hard and rigid. When heated, it gradually softens, and at 120° C. (248° F.) begins to melt; when it is fused, it remains greasy and semi-fluid after cooling, but if exposed to the air in thin layers, gradually dries up and recovers its original properties, provided it has not been heated much above its melting point. If, however, it be heated to 200° C. (398° F.) it begins to fume, and is converted into a viscid mass which no longer dries up. If mixed in this state with half its weight of lime slaked to powder, it forms a tenacious non-drying cement, which serves admirably for attaching glass-plates to vessels with ground lips, such as are used for preserving anatomical preparations, as it forms an air-tight, but easily-loosened joint; if a drying cement be required, a quantity of red lead may be added equal in weight to the lime.

According to the experiments of Ure (Phil. Trans. 1822), confirmed by those of Faraday (Quart. Journal of Sc. Lit. and Art, xi. 19), caoutchouc is composed wholly of carbon and hydrogen, containing 87·5 per cent. of carbon, and 12·5 hydrogen. It is not, however, a simple proximate principle, but chiefly a mixture of two substances, one much more soluble in ether, benzene, and other liquids than the other.

On examining with the microscope a thin sheet of caoutchouc, it is seen to be filled with irregularly rounded pores, partly communicating with each other, and dilating under the influence of liquids. It is perfectly insoluble in water and alcohol; but ether, benzene, rock-oil, and sulphide of carbon, penetrate it rapidly, causing it to swell up and apparently dissolving it.

The liquid thus formed, is not, however, a complete solution, but a mixture formed by the interposition of the dissolved portion between the pores of the insoluble substance, which is considerably swelled up, and has thus become easy to disintegrate. By employing a sufficient quantity of these solvents, renewed from time to time, without agitation, so as not to break the tumefied portion, the caoutchouc may be completely separated into two parts, viz. a substance perfectly soluble, ductile, and adhering strongly to the surface of bodies to which it is applied; and another substance, elastic, tenacious, and sparingly soluble. The proportions of these two principles vary with the quantity of the caoutchouc and the nature of the solvent employed. Anhydrous ether extracts from amber-coloured caoutchouc 66 per cent. of white soluble matter; oil of turpentine separates from common caoutchouc 49 per cent. of soluble matter having a yellow colour.

The best solvent for caoutchouc is a mixture of 6 to 8 pts. of absolute alcohol and 100 pts. of sulphide of carbon. (Payen.)

Caoutchouc is not altered by dilute acids. Strong sulphuric acid acts slowly, and fuming nitric acid rapidly on it, the latter with complete decomposition. It resists strong alkaline-leys, even at the boiling heat.

Caoutchouc yields by *dry distillation*, an empyreumatic oil called oil of caoutchouc or caoutchoucin, which forms an excellent solvent for caoutchouc and other resins. It is a mixture of a considerable number of hydrocarbons. Ordinary impure caoutchouc likewise yields small quantities of carbonic anhydride, carbonic oxide, water, and ammonia.

Respecting the nature of the hydrocarbons contained in caoutchouc-oil, different experimenters have arrived at somewhat different results. According to Bouchardat (J. Pharm. xxiii. 457), the most volatile of the hydrocarbons has a density of 0·63 at −4° C.; boils at a temperature above 0° C., is not solidified by cold, and is perhaps identical with tetrylene, C^4H^8. The next, caoutchene, isomeric with the first, has a density of 0·65, boils at 14·5° C., and solidifies at −15° in brilliant needles which melt at −10°.

The less volatile portion of the oil, which does not distil till the temperature is raised to 315° C. and does not solidify at the lowest temperatures, is called heveene. It is a clear yellow oil of specific gravity 0·921 at 19° C. and belonging to the camphene group, C^nH^{2n}. It mixes with alcohol and ether, absorbs chlorine quickly, and solidifies to a waxy mass. By repeated treatment with strong sulphuric acid and potash-ley, it is converted into an oil, boiling at 228° C., having a sweeter and more agreeable taste than heveene, and similar in many respects to eupione. (Bouchardat.)

Himly (Phil. Mag. [3] lvi. 579), by subjecting caoutchouc-oil to repeated fractional distillation, obtained: 1. An oil called *Faradayin*, boiling at 33° C., of specific gravity 0·654, and dissolved by strong sulphuric acid without evolution of sulphurous anhydride. According to Liebig, water separates from this solution a colourless oil boiling at 220° C. According to Gregory, both this and the more volatile oils belong to the group of camphenes, C^nH^{2n}. The oil unites with chlorine and bromine, forming brown liquids.—2. A mixture of oils distilling at 96° C. from which potash extracts creosote, and dilute sulphuric acid separates a brown resin, destroying the odour at the same time. According to Himly, the percentage of carbon in these oils increases as the boiling point rises.—3. Caoutchin (p. 736).

Another hydrocarbon, isoprene, polymeric with caoutchin, and boiling at 37—38° C., has been obtained by Gr. Williams (Proc. Roy. Soc. x. 56), from the distillation of caoutchouc. From the composition of these several hydrocarbons, it appears that the decomposition of caoutchouc by heat is merely the disruption of a hydrocarbon into other compounds polymeric with it.

The residue left in the retort, after the volatile oil of caoutchouc has distilled off, forms, when dissolved in the oil, a varnish much used by shipwrights, being impervious to moisture and very elastic. An exceedingly tenacious glue is also made by dissolving 1 pt. of caoutchouc, cut up into small pieces, in 4 pts. of coal-tar, adding 2 pts. of shellac when the solution is complete, and heating the whole in an iron vessel.

VULCANISED CAOUTCHOUC.—When caoutchouc is kneaded in an iron box with flowers of sulphur heated to about 112° C. (234° F.), it takes up a certain portion of sulphur, and acquires new properties which greatly increase its utility for various purposes in the arts. It remains perfectly flexible at temperatures below 0° C. and does not soften at 50° C. (122 F.), whereas ordinary caoutchouc becomes perfectly rigid at temperatures several degrees above the freezing point, while a moderate heat renders it so soft and adhesive as to be useless. This sulphured or *vulcanised* caoutchouc, is an excellent material for tubes for conveying water or gases, or for bags to hold gases under pressure.

The vulcanisation of caoutchouc requires a temperature of about 150° C. (304° F.), maintained for a few minutes only. A longer contact with sulphur at that temperature causes the caoutchouc to absorb too much, which renders it hard and brittle. Vulcanised caoutchouc appears to retain only one or two-hundredths of its weight of sulphur in the state of combination; a larger quantity, 15 or 20 per cent., remains simply interposed between the pores, and may be extracted either by the action of solvents, such as ether, benzene, and sulphide of carbon, or by friction, or alternate extension and contraction. If the vulcanised caoutchouc be heated to 120° C., this mechanically interposed sulphur enters into combination with the caoutchouc and renders it brittle. The same combination takes place slowly at ordinary temperatures, so that the caoutchouc after some time, loses its elasticity and becomes brittle. By contact with certain metals, such as lead or silver, the free sulphur in the pores of the caoutchouc is abstracted, and thus again the quality is deteriorated.

The vulcanisation of caoutchouc is effected in various ways: 1. By immersing the sheet-caoutchouc in flowers of sulphur heated to 112° C. till it has absorbed about $\frac{1}{13}$ of its weight, and then heating it for a short time to 150° C., or by immersing the caoutchouc in flowers of sulphur heated to 150°, and keeping up that temperature till the sulphuration is complete.—2. By immersing the caoutchouc in a mixture of 100 pts. sulphide of carbon, and 2·5 protochloride of sulphur, and then plunging it into water to decompose the excess of chloride of sulphur.—3. By immersing articles of caoutchouc already manufactured, in a solution of polysulphide of calcium marking 25° Baumé, keeping them in it for three hours in a closed vessel at 140° C., and then washing them with weak alkaline-ley of 60° Bm. This process always yields the right amount of sulphuration.—4. By powdering 100 pts. of the caoutchouc in rough laminæ, with a mixture of 4 pts. flowers of sulphur and 50 pts. slaked lime, pressing it between rollers so as to incorporate it thoroughly with the powder, then working it into various fabrics by the usual processes, and exposing the finished articles for an hour to the action of vapour of water. By this last treatment, the surface of the caoutchouc experiences a kind of washing, which removes the excess of sulphide of calcium, and brings it to the exact degree of sulphuration required.

Hardened Caoutchouc. Ebonite. — Caoutchouc may be hardened and rendered susceptible of polish by mixing it in the kneading machine or between rollers, with half its weight of sulphur, rolling the mass into sheets, and heating it for two hours to 100° C., and then for four hours to 150°. At the latter temperature, the mass may be rolled; when cold it may be cut like ivory. It serves for the manufacture of combs, knife-handles, buttons, &c. It is also preeminently distinguished by the large quantity of electricity which it evolves when rubbed, and is therefore admirably adapted for the plates of electrical machines. It resists the action of solvents even more obstinately than elastic vulcanised caoutchouc, scarcely even swelling up when immersed in sulphide of carbon. (For a full account of the manufacture and use of caoutchouc, both ordinary and vulcanised, see *Ure's Dictionary of Arts, Manufactures and Mines*, i. 581—604. *Muspratt's Chemistry*, p. 441—451. Payen, *Précis de Chimie Industrielle*, 4^{me} éd. i. 139—184. *Handw. d. Chem.* 2^{te} Aufl. ii. [2] 836—853.)

CAOUTCHOUC, MINERAL. See ELATERITE.

CAOUTCHOUCIN. Empyreumatic oil of caoutchouc (p. 739).

CAPERS. See CAPPARIS.

CAPHOPICRITE. Syn. of RHEIN or RHABARBARIN.

CAPILLARITY. The surface of a liquid at rest is horizontal, excepting where it comes in contact with the sides of the vessel; there it is curved, being concave if the liquid wets the vessel, convex in the contrary case. Moreover, if one end of a narrow tube be dropped into the liquid, the level of the liquid within the tube is not the same as that without, but higher if the liquid wets the vessel and assumes a concave surface, lower if it does not wet the vessel and forms a convex surface; thus water, alcohol, ether, oils, &c., rise in narrow tubes of glass, metal, or wood, having the inner surface clean; but if the surface is greased so that the liquid cannot wet it, depression takes place instead of elevation: mercury is also depressed in tubes of glass, but rises in a tin tube, to which it can adhere. The phenomenon is called capillarity (from *capilla*, a hair), because it is most conspicuous in tubes of very fine bore. The term is, however, extended to all the alterations of level and form of surface which take place at the contact of liquids and solids. The curved surface of the liquid within the tube is called a meniscus.

The amount of elevation of a liquid in capillary tubes is measured by reading off with the cathetometer (a telescope moving up and down a vertical scale, p. 274), first the height of the lowest point of the meniscus, then the height of a fine metallic point brought exactly in contact with the surface of the liquid. In making this last observation, the point is brought down to the surface of the liquid, till it exactly coincides with its reflected image therein, and a small quantity of the liquid is then removed with a pipette so as to leave the extremity free. Another mode of observation, adopted chiefly for measuring the depression of mercury in glass tubes, is to place the liquid in a syphon-tube one arm of which is of capillary bore, while the other is wide enough to render the alteration of level due to capillarity imperceptible. The difference of level in the two arms is then read off with the cathetometer.

By these methods it has been found that the elevation or depression of liquids in capillary tubes is regulated by the following laws:

1. In a tube of given diameter, the amount of elevation or depression depends upon the nature of the liquid, and not at all upon the nature or the thickness of the material of the tube, the nature of the tube merely determining whether the liquid shall be elevated

or depressed, according as the tube is or is not wetted by it, but not affecting the amount.

2. The amount of elevation or depression varies with the temperature, but not according to the same law as the density. Thus Gay-Lussac found that in a tube of 1 millimetre diameter, the heights to which alcohol rose varied with the temperature and density, as follows:

Density.	Temperature.	Height of Column.
0·8196	8° C.	12·18 mm.
0·8135	16 „	9·15 „
0·8595	10 „	12·01 „
0·9415	8 „	12·91 „

3. In very narrow cylindrical tubes, the amount of elevation or depression of a given liquid varies inversely as the diameter of the tube.

4. In the annular space enclosed between a wide cylindrical tube, and a solid cylinder which nearly fills it, the height to which a liquid rises is *half* that to which it would rise in a cylindrical tube whose diameter is equal to the thickness of the annular space. Hence also between two parallel flat plates, which may be regarded as cylinders of infinite radius, the height to which a liquid rises is half that in a cylindrical tube whose diameter is equal to the width between the plates.

The following table shows the height, as determined by Frankenheim (Pogg. Ann. lxx. 515), to which different liquids rise in cylindrical tubes of 1 millimetre radius at 25° C.

	Specific Gravity.	Height in millim.		Specific Gravity.	Height in millim.
Benzene	0·840	6·60	Water	0·997	14·67
Oil of turpentine	0 871	6·33	Sulphide of carbon	1·253	4·84
Oil of lemon	0·820	6·63	Trichloride of phosphorus	1·45	3·75
Rock-oil	0·827	6·52	Disulphide of chlorine	1·687	4·95
Oil of cloves	1·030	6·69	Trichloride of arsenic	2·18	4·07
Eupione	0·655	5·72	Dichloride of tin	—	2·50
Alcohol	0·800	5·73	Chloride of nitrogen	1·34	3·9
Ether	0·716	4·77	Bromine	3·0	4·5
Oxalic ether	1·093	6·05	Sulphur	2·14	5·8
Acetic ether	0·749	5·61	Mercury	13·59	—4·6

For the theory of capillary phenomena, we must refer to works on physics (*vid.* Müller, *Lehrbuch der Physik und Meteorologie*, 1853, i. 97).

CAPNOMOR. One of the constituents of beech-tar, first separated by Reichenbach (J. pr. Chem. i. 1). According to Völckel (Ann. Ch. Pharm. lxxxvi. 99), capnomor is contained, together with creosote and another oil, in the portion of wood-tar which is soluble in potash, and on distilling the alkaline-liquid, capnomor passes over with the vapour of water. It is perhaps partly formed by the decomposition of the creosote.

It is a colourless oil, having a peculiar odour, rather lighter than water; boils between 180° and 208° C. Insoluble in pure water and in potash, but dissolves partially when creosote is likewise present. Contains 81·2 carbon and 7·8 hydrogen; perhaps $C^{20}H^{22}O^{2}$. It dissolves in strong sulphuric acid with red-purple colour; the solution is decolorised by water and then contains a conjugated acid. Nitric acid converts it into prussic and oxalic acid and another crystalline substance.

CAPORCIANITE. A silicate of calcium and aluminium found in several localities in Tuscany, both in radiated laminæ and in crystals belonging to the monoclinic system; cleavage perfectly parallel to $0P$ and $\infty P \infty$, easy also parallel to ∞P. It has a flesh-red colour with nacreous lustre; transparent only in thin laminæ. Specific gravity 2·470. Hardness = 3·5. It splits easily into thin acicular fragments. It gives off water when heated in a tube; and melts with intumescence to a white enamel before the blowpipe. Dissolves easily in acids, with separation of gelatinous silica. According to Anderson's analysis (N. Edinb. Phil. J. xxxiv. 21), it contains 52·8 SiO^2, 21·7 Al^4O^3, 0·1 Fe^4O^3, 11·3 Ca^2O, 1·1 K^2O, 0·2 Na^2O, 0·4 Mg^2O and 13·1 H^2O (= 100·7), agreeing nearly with the formula $Ca^2O.Al^4O^3.4SiO^2 + 3\,aq$. It appears to be a variety of Laumontite formed by weathering.

CAPPARIS SPINOSA. A shrub growing in the south of Europe, the root-bark of which is said to contain a neutral bitter principle of sharp irritating taste, and resembling senegin. The flower-buds pickled in salt and vinegar form capers. Distilled with water they yield a distillate having an alliaceous odour. After they have been washed with cold water, hot water extracts from them capric acid and a gelatinous substance of the pectin group. Capric acid is sometimes found deposited on the calices of the buds in white specks having the appearance of wax. (Rochleder and Blas.)

CAPRAL. A term applied sometimes to caproic, sometimes to capric aldehyde (see those compounds).

CAPRAMIDE. *Caprinamide.* $C^{10}H^{21}NO = N.C^{10}H^{19}O.H^{2}$.—The primary amide of capric acid, produced by the action of strong ammonia, on an alcoholic solution of caprate of ethyl. When purified by crystallisation from alcohol, it forms colourless shining crystalline scales, which have a silky lustre when dry, are insoluble in water and in aqueous ammonia, but dissolve readily in alcohol. (Rowney, Ann. Ch. Pharm. lxxix. 231.)

CAPRIC ACID. *Rutic Acid.* $C^{10}H^{20}O^{2}$. (Gm. xiv. 485.)—This acid was first discovered by Chevreul in the butter of cow's milk. It is contained in cocoa-nut oil, and in several kinds of fusel oil; it occurs among the products of the distillation of oleic acid and of choloïdic acid, and is also formed by the oxidation of oleic acid and of oil of rue.

According to Rowney, it is obtained pure and in tolerable quantity from the residue which remains in the distillation of fusel oil, after the amylic alcohol has distilled off at 132° C. The caproic acid is present as caprate of amyl. When this residue is decomposed by boiling with caustic potash, the amylic alcohol distils over, and the residue contains caprate of potassium. On the addition of hydrochloric acid, capric acid is liberated as an oily mass, which is washed with water and dissolved in dilute ammonia. The caprate of ammonium is mixed with chloride of barium, and the insoluble barium-salt which precipitates is filtered off, washed with cold, and dissolved in boiling water: on cooling, caprate of barium is deposited almost pure. To obtain the acid, this salt is treated with carbonate of sodium, and the solution of caprate of sodium is filtered from the carbonate of barium, then decomposed with sulphuric acid, which throws down capric acid almost colourless, and in the solid form. It is purified by solution in alcohol and reprecipitation by water.

The CAPRATES are mostly difficultly soluble in water.

Caprate of Barium, $C^{10}H^{19}BaO^{2}$, is almost insoluble in cold, but soluble in boiling water, from which it separates in needle-shaped or large prismatic crystals, which float on water if not moistened.

Caprate of Calcium, $C^{10}H^{19}CaO^{2}$, falls as a white insoluble powder when caprate of ammonium is mixed with chloride of calcium. It is more difficultly soluble in boiling water than the barium-salt, and crystallises in beautiful lustrous laminæ.

Caprate of Magnesium resembles the calcium-salt.

Caprate of Lead is precipitated as a white amorphous powder when caprate of sodium is mixed with acetate of lead. It is very little soluble in boiling alcohol.

Caprate of Silver is precipitated on the addition of nitrate of silver to caprate of ammonium. It is but slightly soluble in boiling water, and is deposited on cooling in needle-shaped crystals. When moist, it is readily changed by exposure to light.

Caprate of Sodium is readily soluble in water and alcohol. On evaporation it is obtained as a horny mass, presenting traces of crystallisation. It is easily soluble in hot absolute alcohol, forming an opalescent mass.

Caprate of Ethyl. Capric ether, $C^{10}H^{19}(C^{2}H^{5})O^{2}$, is formed by dissolving capric acid in absolute alcohol, saturating the solution with dry hydrochloric acid gas, and then mixing with water. It separates as an oily layer, which, when washed with water, forms a colourless liquid of specific gravity 0·862. E. A.

CAPRIC ALDEHYDE. $C^{10}H^{20}O$.—The aldehyde of capric acid has not yet been obtained with certainty. It was formerly supposed, according to the results of Gerhardt (Ann. Ch. Phys. [3] xxiv. 96) and Wagner (J. pr. Chem. xlvi. 155; lii. 48), to be the chief constituent of oil of rue, but according to Gr. Williams (Phil. Trans. 1858, p. 199), this oil consists mainly of *euodic aldehyde*, $C^{11}H^{22}O$. This result, so far as regards the quantitative constitution, has been confirmed by Hallwachs (Ann. Ch. Pharm. cxiii. 107), who, however, maintains that the body $C^{11}H^{22}O$ is not an aldehyde. According to more recent statements by Wagner, on the contrary, oil of rue is really capric aldehyde, and forms with ammonia a compound which, when treated with sulphydric acid, yields *thiocapric aldehyde*, $C^{30}H^{61}S^{2}N$, and with hydrochloric and hydrocyanic acid a compound homologous with alanine. (See RUE, OIL OF.) (Handw. d. Chem. 2^te Aufl. ii. [2] 741.)

CAPRINAMIDE. See CAPRAMIDE.

CAPROCIANITE. Syn. with CAPORCIANITE.

CAPROENE. Syn. with HEXYLENE, $C^{6}H^{12}$.

CAPROIC ACID. $C^6H^{12}O^2$. (Gm. xi. 414.)—This acid, the sixth in the series of fatty acids, was first discovered by Chevreul in the butter of cow's milk, in which it exists in combination with glycerin. It exists in considerable quantity in cocoa-nut oil, and in cheese, and is a not unfrequent product of the oxidation of the fatty acids of higher atomic weight; it is also obtained by the oxidation of poppy oil and of casein.

From cocoa-nut oil it is readily obtained by saponification with soda-ley of specific gravity 1·12. The soap is decomposed by sulphuric acid, and rapidly distilled from a copper retort. The distillate, which consists essentially of caproic and caprylic acids, is neutralised with baryta, and the solution evaporated to crystallisation. The crystals which first form are caprylate of barium; when the solution is further evaporated and allowed to stand, caproate of barium is obtained in verrucose crystals. The salt purified by crystallisation and decomposed by a stronger acid, yields caproic acid in an oily form.

The best method of preparation is that of Frankland of Kolbe, viz. the decomposition of cyanide of amyl by potash:

$$\underset{\substack{\text{Cyanide}\\ \text{of amyl.}}}{C^6H^{11}N} + KHO + H^2O = \underset{\substack{\text{Caproate of}\\ \text{potassium.}}}{C^6H^{11}KO^2} + \underset{\text{Ammonia.}}{NH^3}.$$

The process as modified by Wurtz, is as follows:—To prepare cyanide of amyl, the black mass obtained by calcining ferrocyanide of potassium in a covered crucible, is placed in a retort connected with the lower part of a Liebig's condenser, together with four or five times its weight of alcohol, and the mixture is heated to boiling. A quantity of iodide of amyl, not quite sufficient to decompose the cyanide, is then gradually introduced through a funnel-tube, and the boiling is continued till the decomposition is complete. This point is ascertained by allowing a drop of the oil which separates on the addition of water, to evaporate on the end of a glass rod held in a flame: the presence of the smallest quantity of iodide is perceptible by the brown vapours of iodine produced. When the conversion of the iodide is effected, the alcoholic liquor is mixed with excess of water, and the oil which separates is boiled with alcoholic solution of potash in a retort connected with the lower end of a Liebig's condenser, until it is completely decomposed into ammonia and caproic acid. The caproate of potassium is then decomposed by a stronger acid, and the oily layer removed and distilled.

Caproic acid is a clear mobile oil of specific gravity 0·931 at 15° C. It has a sudorific odour and penetrating acid taste. Sparingly soluble in water, but dissolves completely in absolute alcohol. The acid prepared from cyanide of amyl solidifies at −9° C., and boils at 198°, and according to Wurtz, has the property of circular polarisation. That from cocoa-nut oil boils between 202° and 209° (probably owing to an admixture of caprylic acid), and does not affect the plane of polarisation.

Caproic acid is dissolved by sulphuric acid without change in the cold, and is again liberated on the addition of water. A concentrated solution of caproate of potassium, when subjected to a current from six of Bunsen's elements, is electrolysed in a manner analogous to valerate of potassium. The oil which separates on the surface contains amyl, $C^{10}H^{22}$, together with another body, which is probably caproate of amyl, resulting from a secondary decomposition:

$$\underset{\substack{\text{Caproate of}\\ \text{potassium.}}}{2C^6H^{11}KO^2} + O = \underset{\text{Amyl.}}{C^{10}H^{22}} + \underset{\substack{\text{Carbonate}\\ \text{of potassium.}}}{K^2CO^3} + CO^2.$$

$$\text{or } \underset{\substack{\text{Caproate of}\\ \text{potassium.}}}{2C^6H^{11}KO^2} + O + H^2O = \underset{\text{Amyl.}}{C^{10}H^{22}} + \underset{\substack{\text{Acid carbonate}\\ \text{of potassium.}}}{2KHCO^3}.$$

CAPROATES.—The salts of capric acid resemble the valerates, and are obtained in a similar manner.

Caproate of Ammonium, obtained by saturating caproic acid with ammoniacal gas, is a crystalline salt, which, by absorbing more ammonia, again deliquesces.

Caproate of Barium is obtained by saturating the acid with carbonate of barium. By spontaneous evaporation of the solution below 18° C. it crystallises in lustrous hexagonal laminæ, which become milky in the air. Crystallised above 30° C. it forms needles often of some length. It dissolves in 12·5 pts. of water at 20° C. In moist air it smells of caproic acid, and its aqueous solution deposits a basic salt when boiled. When distilled it yields combustible gases, among which propylene, C^3H^6, is present in greatest quantity, and an oil passes over which contains propione, $C^{11}H^{22}O$. The residue consists of carbonate of barium and charcoal.

Caproate of Calcium forms lustrous square laminæ, which are soluble in 49 pts. of water at 14° C., and fuse on being heated, emitting an odour like that of the *Labiatæ*.

Caproate of Magnesium, $C^6H^{11}MgO^2 + aq.$, crystallises in small aggregated needles, which retain 1 at. of water when heated above 100° C.

Caproate of Potassium, $C^6H^{11}KO^2$, is obtained by the spontaneous evaporation of its solution, as a transparent jelly, which becomes opaque when warmed.

Caproate of Silver, $C^6H^{11}AgO^2$, is obtained by precipitating an aqueous solution of the barium-salt with nitrate of silver, as a white precipitate, sparingly soluble in cold water. After being washed out with cold, and then dissolved in boiling water, it separates on cooling in magnificent crystalline laminæ, which are unaltered by light.

Caproate of Sodium, $C^6H^{11}NaO^2$, resembles the potassium-compound. Its aqueous solution forms a white uncrystalline mass on evaporation.

Caproate of Strontium, $C^6H^{11}SrO^2$, crystallises in transparent laminæ, which effloresce in the air. E. A.

CAPROIC ALCOHOL. See HEXYLIC ALCOHOL.

CAPROIC ALDEHYDE. *Hydride of Caproyl.* $C^6H^{12}O = C^6H^{11}O.H.$—This compound appears to be produced in small quantity in the dry distillation of caproate of calcium or barium, being found chiefly in the first portion of the distillate obtained by the rectification of crude caprone. (Brazier and Gossleth, Ann. Ch. Pharm. lxx. 256.)

CAPROIC ANHYDRIDE or *Anhydrous Caproic Acid.* $C^{12}H^{22}O^3 = (C^6H^{11}O)^2O.$—According to Chiozza, this body is prepared by placing 6 at. caproate of barium in a retort, and gradually adding 1 at. oxychloride of phosphorus. The mass becomes warm and pasty; on cooling it is extracted with pure ether; the ethereal solution is agitated with weak potash, then dried over chloride of calcium; and finally the ether is evaporated in the water-bath.

Caproic anhydride is a neutral oil, lighter than water, and with an odour resembling caproic acid. When heated it volatilises, emitting an aromatic odour, and leaving a slight carbonaceous residue. E. A.

CAPROIC ETHERS. *Caproate of Methyl*, $C^6H^{11}(CH^3)O^2$, is obtained, according to Fehling, by mixing 2 pts. each of caproic acid and of wood-spirit with 1 pt. of sulphuric acid, and gently heating the mixture. The liquid is mixed with water, and the supernatant oil is washed with water and dried over chloride of calcium. It is a colourless liquid of specific gravity 0·8977 at 18° C.; boils at 150° C. Its vapour-density is 4·623.

Caproate of Ethyl, $C^6H^{11}(C^2H^5)O^2$, is obtained like the preceding compound. It is a transparent liquid, with a pine-apple odour, somewhat resembling butyric ether, but not so delicate. Its specific gravity is 0·882 at 18° C., and it boils at 162° C. Its vapour-density is 4·97.

Caproate of Amyl. $C^6H^{11}(C^5H^{11})O^2$.—Crude caproic acid (prepared by Frankland and Kolbe's method), the greater part of which passes over at 198° C., contains an admixture of caproate of amyl. On continuing the distillation, it passes over at 212° C. It may also be obtained by neutralising the crude acid with carbonate of potassium, whereupon it remains undissolved as an oily layer. Removed, dried over chloride of calcium, and rectified, it is obtained pure, and of constant boiling point at 211° C. It is insoluble in water, but soluble in all proportions in alcohol and ether. It is decomposed by potash into caproate of potassium and amylic alcohol. E. A.

CAPRONE. $C^{11}H^{22}O$? When caproate of barium is submitted to destructive distillation, tritylene and other gases are given off, and a colourless oil passes over. If this oil be dried and rectified, it begins to boil at 120° C., and the thermometer ultimately rises to 160°—170° C. By rectification, a product is obtained, boiling constantly at 165° C. It is a colourless oil, lighter than and insoluble in water, and having a peculiar odour. It is readily soluble in alcohol and ether, becomes brown in the air, and is attacked by nitric acid even in the cold, *nitrovaleric acid*, $C^5H^9(NO^2)O^2$, being apparently formed.

The boiling-point of this compound (164° C.), differs widely from that calculated for caprone, 232°, and it is hence doubtful whether it is the true caprone.

CAPRONITRILE. $C^6H^{11}N$. This compound, which contains the elements of caproate of ammonium *minus* water $[C^6H^{11}(NH^4)O^2 - 2H^2O]$, has not been obtained directly from that salt. The isomeric (or identical) compound, cyanide of amyl, $C^5H^{11}.CN$, is obtained by heating an alcoholic solution of iodide of amyl to the boiling point, with excess of cyanide of potassium. (See CYANIDES OF ALCOHOL-RADICLES.)

CAPRONOYL. A name applied by Weltzien to the radicle C^6H^{11}, which may be supposed to exist in caproic aldehyde, $C^6H^{11}.H.O$, and in caprone, $C^6H^{11}.C^5H^{11}.O$.

CAPROYL (or *Capronyl*, according to Weltzien), $C^6H^{11}O$.—The radicle of caproic acid and its derivatives: *e. g.* caproic acid = $C^6H^{11}O.H.O$; caproic aldehyde, $C^6H^{11}O.H$;

caprone, $C^6H^{11}O.C^5H^{11}$, &c. The same term is also sometimes applied to the corresponding alcohol-radicle C^6H^{13}; but it is much better to designate this radicle by the name Hexyl, as proposed by Gerhardt. (See Hexyl.)

CAPROYLAMINE. See Hexylamine.

CAPROYLENE. See Hexylene.

CAPRYL or **RUTYL,** $C^{10}H^{19}O$. — The radicle of capric or rutic acid, $C^{10}H^{19}O.H.O$, and its derivatives. The same term is applied to $C^8H^{15}O$, the radicle of caprylic acid: it is better however to call the latter caprylyl, unless indeed the term capric acid be altogether abandoned, and rutic acid substituted for it. $C\,^0H^{19}O$ would then be called rutyl, and $C^8H^{15}O$, capryl. There is at present great confusion between the names of these radicles, which is further increased by the application of the same name, *capryl*, to C^8H^{17}, the radicle of the 8-carbon alcohol. For this last-mentioned radicle we shall use Gerhardt's name Octyl (*q. v.*)

CAPRYLAMINE. See Octylamine.

CAPRYLENE. See Octylene.

CAPRYLIC ACID. $C^8H^{16}O^2 = C^8H^{15}O.H.O$ (Gm. xiii. 190).—Caprylic acid was discovered by Lerch, in the butter of cow's milk. It is also contained in cocoa-nut oil and in Limburg cheese; in several kinds of fusel oil it occurs partly free and partly in combination with ethyl and amyl.

The best source for this acid is cocoa-nut oil: from the difficult solubility of its barium salt, it is easily separated from caproic acid, with which it is associated (see Caproic Acid). The caprylate of barium is purified by recrystallisation; its aqueous solution decomposed by sulphuric acid; and the oily liquid which rises to the surface is washed and distilled: the distillate between 230 and 238° C. is pure caprylic acid.

Caprylic acid has a feeble but unpleasant odour, which is more perceptible when the acid is warm. It solidifies at 12° C., melts at 15°, and as the liquid slowly cools, laminæ resembling cholesterin form in it. At 20°, its specific gravity is 0·911. It boils at 236°—238°; its observed vapour density is 5·31 (calculated 4·98).

Caprylic acid is monobasic, the general formula of its salts being $C^8H^{15}MO^2$. *Caprylate of Barium*, $C^8H^{15}BaO^2$, crystallises from a hot aqueous solution, in fine, white, fatty laminæ; by spontaneous evaporation, in small white grains. It dissolves in 50 pts. water at 100° C., and in 126 pts. at 10°. It is quite insoluble in alcohol and ether. It contains no water of crystallisation, and can be heated to 100° without change.

Caprylate of Lead, $C^8H^{15}PbO^2$, is obtained on mixing caprylate of barium with nitrate of lead. Is a sparingly soluble precipitate, which melts at 100° C.

Caprylate of Silver, prepared in the same manner, is white and insoluble. E. A.

Substitution-derivative of Caprylic Acid.

Nitrocaprylic Acid. $C^8H^{15}NO^4 = C^8H^{14}(NO^2)O^2$ (Wirz, Ann. Ch. Pharm. civ. 289).—This acid is produced by the continued action of nitric acid at the boiling heat on the mixture of non-volatile fatty acids which is obtained from cocoa-nut oil by saponifying the oil with soda, decomposing the soap with sulphuric acid, and distilling off the volatile acids. After washing the product with hot water, till the grains of suberic acid mixed with it are removed, there remains a heavy oil, containing nothing but nitrocaprylic and nitrocapric acids. The acid thus obtained is a yellowish-red, syrupy oil, having a peculiar odour and bitter taste, of specific gravity 1·093, at 18° C.; it dissolves sparingly in water, more easily in strong nitric acid. When heated, it becomes dark-coloured, and decomposes, with evolution of nitrous acid, and at a higher temperature, detonates slightly.

Nitrocaprylic acid neutralises alkalis completely. With ammonia, it forms a yellowish-red, and with potash a deep red solution, leaving an uncrystallisable mass when evaporated. The ammonia-salt yields with salts of calcium, barium, lead, and copper, flaky precipitates, which form a viscid mass when stirred. The silver-salt, $C^8H^{14}Ag(NO^2)O^2$ is precipitated in yellowish-white flakes, which dry up to a yellowish-grey mass.

CAPRYLIC ALCOHOL. See Octylic Alcohol.

CAPRYLIC ALDEHYDE. *Hydride of Caprylyl*, $C^8H^{16}O = C^8H^{15}O.H$.—A body having this composition and capable of uniting with the acid sulphites of alkali-metals, is obtained, among other products, by the dry distillation of castor-oil soap (ricinoleate of sodium or potassium), either alone or with excess of alkali. It was first obtained by Limpricht (Ann. Ch. Pharm. xciii. 242), who regards it as caprylic aldehyde; afterwards examined by Bouis (Ann. Ch. Phys. [3] xlviii. 99), who takes the same view of its constitution; and further by Städeler (J. pr. Chem. lxxii. 241), and by

Dachauer (Ann. Ch. Pharm. cvi. 270), who regard it as an acetone, viz. methyl-œnanthyl, $CH^3.C^7H^{13}O$. According to Bouis, the aldehyde is formed, together with an acid ($C^{10}H^{18}O^2$), and without evolution of gas, chiefly when castor-oil soap is slowly heated to a temperature not exceeding 225°—230° C., and without excess of alkali:

$$\underset{\text{Ricinoleic acid.}}{C^{18}H^{34}O^3} = \underset{\text{Caprylic aldehyde.}}{C^8H^{16}O} + \underset{\text{New acid.}}{C^{10}H^{18}O^2};$$

whereas if the soap be quickly and strongly heated, especially with excess of alkali, hydrogen is abundantly evolved, and octylic alcohol is produced, together with sebacic acid (see page 98). Malaguti obtained sometimes octylic alcohol, sometimes caprylic aldehyde, but always sebacic acid; he explains the formation of these products by the equations:

$$\underset{\text{Ricinoleic acid.}}{C^{18}H^{34}O^3} + H^2O + O = \underset{\text{Octylic alcohol.}}{C^8H^{18}O} + \underset{\text{Sebacic acid.}}{C^{10}H^{18}O^4}$$

$$C^{18}H^{34}O^3 + O^2 = \underset{\text{Caprylic aldehyde.}}{C^8H^{16}O} + C^{10}H^{18}O^4$$

Städeler and Dachauer likewise obtained sebacic acid in every case (p. 98).

Caprylic aldehyde is also produced by distilling a mixture of caprylate and formate of calcium (Limpricht):

$$\left.\begin{matrix} C^8H^{15}O \\ Ca \end{matrix}\right\} O + \left.\begin{matrix} CHO \\ Ca \end{matrix}\right\} O = Ca^2CO^3 + \left.\begin{matrix} C^8H^{15}O \\ H \end{matrix}\right\}$$

To prepare pure caprylic aldehyde, the crude distillate obtained by heating castor-oil soap with excess of hydrate of potassium, is treated with a strong aqueous solution of acid sulphite of sodium; and the resulting crystalline mass is repeatedly pressed between paper, washed with alcohol, dried over sulphuric acid, and dissolved in hot water, whereby it is decomposed, and caprylic aldehyde set free: it is then dried over chloride of calcium and rectified. According to Bouis, it is better to distil the neutral soap *per se*, or better still, the barium-salt formed from it, because the latter does not froth.

Caprylic aldehyde is a colourless, strongly refracting liquid, having an aromatic odour and caustic taste. Specific gravity 0·818 at 19° C. (Bouis). Boiling point 178° (Limpricht); 171° under ordinary pressure (Bouis). It is insoluble in water. It burns with a bright non-smoking flame; becomes acid when warm air or oxygen is passed through it (Bouis); and is violently oxidised by nitric acid, with formation of caprylic acid and other fatty acids; chromic acid also partly converts it into an acid. Heated with solid potash, it forms a brown spongy mass. With ammoniacal nitrate of silver it forms a metallic mirror. With pentachloride of phosphorus, it forms chloride of octylene, $C^8H^{16}Cl^2$.

Caprylic aldehyde unites with acid sulphites of alkali-metals, without rise of temperature. The compounds are insoluble in excess of the acid sulphite, and are decomposed by water. The sodium-salt contains $2C^8H^{16}O.2NaSO^3.SO^2 + 2\,aq.$

CAPRYLIC ANHYDRIDE. *Anhydrous Caprylic acid*, $C^{16}H^{30}O^3. = (C^8H^{15}O)^2O$. —This body is obtained by treating 6 at. caprylate of barium with 1 at. of oxychloride of phosphorus. Much heat is disengaged, and the mixture is changed into a pasty mass, developing a peculiar and unpleasant odour, which probably arises from chloride of caprylyl. From this pasty mass, the anhydride is extracted by treatment with ether, which must be free from alcohol. The ethereal solution is agitated with dilute potash-ley, in order to remove caprylic acid, and then dried over chloride of calcium. On the evaporation of the ethereal solution, the anhydride is left as a clear mobile oil, lighter than water. When freshly prepared, it has a sickly odour, which is more evident when it begins to pass into caprylic acid. When heated, it gives off vapours which attack the throat, but have an aromatic odour. In a freezing mixture, it solidifies to a white mass of imperfectly crystalline texture. It begins to boil at 280° C., the temperature gradually increasing to 290°, when the liquid begins to decompose. Boiling water does not convert it into caprylic acid, but when left for some time in contact with moist air, it gradually changes into that substance. Potash-ley gradually changes it into caprylic acid. (Chiozza, Ann. Ch. Pharm. lxxxv. 229).

E. A.

CAPRYLIC ETHERS. *Caprylate of Methyl.* $C^8H^{15}(CH^3)O^2$, is formed, when caprylic acid dissolved in its own weight of methylic alcohol is mixed with a quarter of the weight of sulphuric acid. The liquid immediately becomes turbid, and the caprylate of methyl forms a light oily layer on the surface. It is removed, washed with water, and dried. It is a colourless, highly aromatic liquid, with an odour of wood-spirit. Its specific gravity is 0·882, and vapour-density 5·48. It is scarcely soluble in water, but dissolves readily in alcohol and in ether. (Fehling, Ann. Ch. Pharm. liii. 405.)

Caprylate of Ethyl, $C^8H^{15}(C^2H^5)O^2$, is prepared like the preceding compound. It is a colourless liquid, with a pine-apple odour. Its specific gravity is 0·8738 at 15°. It boils at 214° C. Vapour-density = 6·1. It is insoluble in water, but soluble in alcohol and ether. (Fehling). E. A.

CAPRYLONE. This name has been given to a substance which Guckelberger obtained by the destructive distillation of caprylate of barium, in quantities of about half an ounce, with excess of lime. White vapours pass off, and condense in the receiver to a yellow oily liquid, which after some time solidifies to a yellow buttery mass. By appropriate purification, it is obtained as a white crystalline body, like Chinese wax, and of feeble waxy odour. It is very soluble in alcohol and ether, whether hot or cold. It melts at 40° C., and solidifies at 38° to a radiating crystalline mass. It boils at 178°, and distils without alteration.

The boiling-point of caprylone, as calculated from that of its homologue œnanthylone, would be 300° C. The discrepancy between this number and 178°, the boiling-point of caprylone, seems to prove that this is not the true acetone. Further experiments are necessary to decide the point. E. A.

CAPRYLYL. $C^8H^{15}O$. The radicle of caprylic acid, &c.

CAPSELLA BURSA PASTORIS. *Shepherd's Purse.*—The green parts of this plant contain an acrid sulphuretted volatile oil (oil of mustard?) waxy and fatty matter, saponin, tannin, tartaric, citric, and malic acids, colouring matter, and traces of sugar. 100 pts. of the air-dried herb yielded 9 per cent. of ash containing sand, the composition of which, in 100 pts., after deducting the charcoal, was found to be: 15·7 K^2O, 8·6 Na^2O, 14·7 Ca^2O, 3·1 Mg^2O, 1·9 Fe^4O^3, 0·1 Al^4O^3, 16·2 CO^2, 6·2 SO^3, 8·4 P^2O^5, 4·2 Cl, 20·6 SiO^2 and sand. (Daubrawa, Repert. Pharm. xcix. 127.)

The seed yields by distillation with water, a volatile oil, which, according to Pless, is identical with oil of mustard. According to G. J. Mulder, the seed contains in 100 pts.: 28·8 fixed oil, 26·5 albumin, 12·3 non-nitrogenous soluble matter, 16·0 woody fibre, 11·6 water, and 4·8 ash. According to Neuburger, the seed contains 20 per cent. of oil and 23 of albumin. (Handw. d. Chem. 2te Aufl. ii. [2] 780.)

CAPSICINE. An alkaloïd obtained from Spanish pepper, the fruit of *Capsicum annuum*. (Braconnot, Ann. Ch. Phys. [2] vi. 1; Witting, Buchner's Repert. xxxvi. 15; Landerer, Vierteljahrs. pr. Pharm. iii. 34.) The same name is applied in America to an oleo-resinous extract from Cayenne pepper (*Capsicum baccatum*).

CAPUT MORTUUM. An old term for the residue of a distillation or sublimation; thus the impure ferric oxide obtained as a residue in the distillation of fuming sulphuric acid from ferrous sulphate, was called *Caput mortuum vitrioli*.

CARAGHEEN MOSS. *Irish pearl moss.* (*Sphærococcus crispus.*)—An alga, found in abundance on the coasts of the Atlantic and the North Sea. It is used as food, as a remedy in chest complaints, and for the clarification of turbid liquids. It swells up considerably in cold water, and dissolves almost wholly on boiling. The decoction forms, on cooling, a jelly having a faint saline taste, and the peculiar odour of sea-weed. According to Herberger, it contains 79·1 per cent. gelatinous matter, partially soluble in cold water, perfectly in hot water, insoluble in alcohol and ether; 9·5 mucus, insoluble in water, alcohol, and ether; 0·7 resin; 1·3 chloride of sodium; 0·7 chloride of magnesium; 8·7 skeleton, consisting of cellular substance and salts.

According to Schmidt (Ann. Ch. Pharm. li. 56), the mucus obtained by precipitating the aqueous decoction with alcohol containing hydrochloric acid, pressing the precipitate, and washing it with alcohol, contains 44·8 carbon to 6·2 hydrogen, (whence it appears to be a hydrate of carbon, like sugar, starch, &c.,) and leaves, when burnt, 10·39 per cent. ash, chiefly consisting of sulphate of calcium. The skeleton of caragheen moss leaves on incineration an ash containing sulphate and phosphate of calcium, and, according to Sarphati, likewise metallic iodides. (Handw. d. Chem. 2te Aufl. ii. [2] 782.)

CARAJURU, CRAJURU, or **CARCURU.** A red dye-stuff, imported from Para in Brazil, probably identical with *chica-red*, which is obtained from the leaves of the *Bignonia Chica*. Carajuru appears, however, to be superior to ordinary chica, and is perhaps distinguished from it by greater purity. According to Virey (J. Pharm. 1844, p. 151) it is a light mealy powder, destitute of taste and smell, and acquiring a coppery lustre by trituration. It is insoluble in water, soluble in alcohol, ether, and alkalis, and precipitated from the latter by acids in its original state. Burns with flame, leaving a considerable quantity of ash.

CARAMEL. (Péligot, Ann. Ch. Phys. lxvii. 172.—Gélis, Ann. Ch. Phys. [3] lii. 352.)—A product of the action of heat upon sugar. When cane-sugar is heated in an oil or metal bath to between 210° and 220° C., care being taken not to exceed the latter temperature, it assumes a brown colour of continually increasing depth, without giving off any permanent gas; vapour of water is, however, evolved, containing traces of acetic acid and an oily substance. When the tumefaction has ceased, the vessel is found to contain a black substance, which dissolves completely in water: this is caramel. To obtain it pure, it is dissolved in a small quantity of water and precipitated by alcohol. It may also be obtained from glucose, but not so readily.

Caramel when pure is insipid; its aqueous solution has a rich sepia tint. It is insoluble in alcohol; does not ferment under the influence of yeast; it yields copious precipitates with ammoniacal acetate of lead and baryta-water. When strongly heated it yields the same products as sugar. (Péligot.)

Caramel was long regarded as a simple proximate principle of the formula $C^{12}H^{18}O^9$, the precipitate which it forms with baryta-water having the composition $C^{12}H^{17}BaO^9$. But, according to Gélis, caramel prepared as above is a mixture of several coloured substances, some soluble, others insoluble in water, amongst which he particularly distinguishes three, viz. *caramelane*, $C^{12}H^{18}O^9$, *caramelene*, $C^{36}H^{50}O^{25}$, and *caramelin*, $C^{96}H^{102}O^{51}$. All these substances are produced from sugar by elimination of the elements of water, the atomic weight being at the same time increased, thus:

$$\underset{\text{Sugar.}}{8C^{12}H^{22}O^{11}} - 37H^2O = \underset{\text{Caramelin.}}{C^{96}H^{102}O^{51}};$$

and by keeping sugar for some time at 190° C. these products may be obtained one after the other. If crystallised cane-sugar be used, the residue, after 10 per cent. has been given off as water, consists of nearly pure **caramelane**; after 14 or 15 per cent. has gone off, the residue is rich in **caramelene**; and after a loss of 20 per cent. it consists almost wholly of **caramelin**. Grape-sugar yields products nearly resembling, but not identical with these.

Caramelane may also be obtained pure by digesting ordinary caramel with 84 per cent. alcohol, which sometimes dissolves it completely, sometimes leaves a residue amounting to 40 per cent; treating the solution (which contains caramelane, undecomposed sugar, and sometimes a little caramelene) with yeast to decompose the sugar by fermentation; evaporating the filtrate to dryness; redissolving in alcohol, which then leaves the caramelene undissolved; and evaporating the solution.

Caramelane, to which ordinary caramel chiefly owes its characteristic properties, is a brown substance, hard and brittle at ordinary temperatures, very soft at 100° C., odourless, with a strong bitter taste, deliquescent, very soluble in water, moderately soluble in aqueous alcohol, sparingly in absolute alcohol, insoluble in ether. It reduces cupric oxide in alkaline solution, also gold and silver from their salts. Nitric acid converts it into oxalic acid. The aqueous solution does not precipitate metallic salts. The alcoholic solution forms, with an alcoholic solution of neutral acetate of lead, a yellow precipitate containing $C^{12}H^{16}Pb^2O^9$; with an ammoniacal solution of acetate of lead, added in sufficient quantity to produce complete precipitation, it yields the compound $C^{12}H^{16}Pb^2O^9.Pb^2O$; and with excess of a solution of baryta in wood-spirit, a precipitate containing $C^{12}H^{16}Ba^2O^9.Ba^2O$. At 190° C. caramelane gives off water and passes into caramelene (**Gélis**). **Völckel** (Ann. Ch. Pharm. lxxxv. 59) applies the term *caramelane* to the black residue, insoluble in water, left on heating sugar to 250°—300° C. This residue is insoluble in alcohol, sparingly soluble in potash, and has, according to Völckel, the composition $C^{24}H^{26}O^{13}$. It is perhaps identical with the substance here called caramelin.

Caramelene. $C^{36}H^{50}O^{25}$.—The residue left after treating caramel with alcohol of 84 per cent. contains caramelene, which may be extracted by cold water, and separated from the solution by evaporation or by precipitation with absolute alcohol, and freed from a small quantity of admixed caramelin by redissolving it in water. It is solid and brittle, of the colour of mahogany, not hygroscopic, easily soluble in water (exhibiting a colouring power six times as great as that of caramelane) and in dilute alcohol, sparingly in strong alcohol, and insoluble in ether. It reduces cupric oxide from an alkaline solution, and is converted by nitric acid into oxalic acid. Its *barium-compound*, precipitated by alcohol, is composed of $C^{36}H^{48}Ba^2O^{25}$. With lead it forms the three compounds $C^{36}H^{48}Pb^2O^{25}$, $C^{36}H^{48}Pb^2O^{25}.3Pb^2O$, and $C^{36}H^{48}Pb^2O^{25}.5Pb^2O$.

Caramelin, $C^{96}H^{102}O^{51}$, exhibits three isomeric modifications, viz. *A*, soluble in water; *B*, insoluble in water, soluble in other liquids; *C*, insoluble in all ordinary solvents. The modifications *B* and *C* are contained in the residues left after treating caramel with cold water; and from these residues *B* may be extracted by boiling water (*B* then passing into *A*) by 60 per cent. alcohol, or by alkaline liquids. Caramelin separates from a hot aqueous solution on evaporation in films, by precipitation with alcohol as a copious precipitate, but in both cases as the modification *B*: similarly when precipitated by acids from alkaline solutions. But when caramelin *B* is dried, or even left for several days in the moist state, it passes into the modification *C*, and is then insoluble in all solvents. Caramelin *B*, which is insoluble in cold water and in strong alcohol, dissolves in a mixture of those two liquids. Its colouring power is 12 times as great as that of caramelane.

Caramelin is a black, shining, infusible substance. Like caramelane, it reduces gold and silver from their solutions, and cupric oxide in its alkaline solution. Its solution is precipitated by nearly all metallic salts. It forms the compounds $C^{96}H^{100}Ba^2O^{51}$, $C^{96}H^{100}Ba^2O^{51}.Ba^2O$, and $C^{96}H^{100}Pb^2O^{51}$. (Gélis.)

Maumené (Compt. rend. xxxix. 422) designates by the name caramelin a black-brown compound, $C^{12}H^8O^4$, insoluble in water, acids and alkalis, obtained by mixing 1 pt. of sugar with 15 to 30 pts. dichloride of tin, evaporating to dryness, and heating for a few minutes to 120°—130° C.; also by similar treatment of glucose, cellulose, dextrin, and other hydrates of carbon of similar constitution. Völckel's caramelane (p. 748) is probably the same as Gélis's caramelin.

CARANNA. A resin obtained from the *Bursera gummifera*. It is sent into the market in pieces wrapped in leaves; is grey-black outside, dark brown within; has a shining fracture; is brittle and easily powdered. It melts when heated, emitting an aromatic smell. It has a bitterish taste. It resembles resin of guaiac in some respects, and was at one time in repute among the Germans for smoking in pipes, as a remedy in gout. A distilled oil of caranna was also prescribed for a like purpose. It is now disused.

CARAPA BARK. The bark of a tree indigenous in Guiana and Hispaniola, called *Carapa guianensis*, *Persoonia guareoides*, and *Xylocarpus Carapa*. It has a bitter taste, like that of cinchona bark, and is used in intermittent fevers. It is said to contain quinic acid, a red colouring matter, and an organic alkaloïd called carapine, which forms crystalline salts with hydrochloric and acetic acids. (Petroz and Robinet, J. Pharm. vii. 293, 349.)

The wood of the same tree, which is beautifully veined, is much prized for furniture.

In the bark of *Carapa tulucana*, Caventou (J. Pharm. xxxv. 189) found one yellow and two red dyes, and a bitter principle, which he calls tulucumine.

The root-bark of *Carapa molucensis* exudes a whitish powder when wounded; it is bitter and astringent, and is said to be used as a remedy against cholera and biliary diseases.

CARAPA OIL. A bitter fat oil, obtained by pressure in the heat of the sun from the kernels of *Carapa guianensis* and *C. tulucana*. It is used by the Indians for protecting the skin against the punctures of insects. It solidifies at + 4° C. and melts at 10°; dissolves sparingly in alcohol, easily in ether; is saponified by alkalis. Its bitter taste is said to be due to strychnine, and to be removed by sulphuric acid. The fruits yield by further pressure, assisted by heat, a fat which melts at 40°—50° C. (Cadet, J. Pharm. v. 49.—Bouillay, *ibid.* vii. 293.)

CARAT. An arbitrary weight by which gold and gems are weighed or estimated. The diamond carat is equal to 4 grains whereof 612 are contained in the troy ounce; in other words, the troy ounce contains 153 diamond carats or 612 diamond-grains.

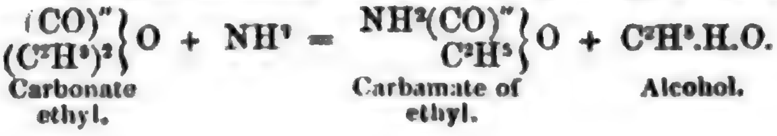
In estimating or expressing the fineness of gold, the whole mass is supposed to weigh 24 carats of 12 grs. each, either real or merely proportional, like the assayer's weights; and the pure gold is called fine. Thus, if gold is said to be 23 carats fine, it is to be understood that in a mass weighing 24 carats, the quantity of pure gold is 23 carats. U.

CARBAMIC ACID. $CH^3NO^2 = \left.\begin{matrix} NH^2(CO)'' \\ H \end{matrix}\right\} O$.—This acid is not known in the free state, neither have any of its metallic salts, properly so-called, been obtained. Its ammonium-salt, $N^2H^6CO^2 = \left.\begin{matrix} NH^2(CO)'' \\ NH^4 \end{matrix}\right\} O$, is the so-called *anhydrous carbonate of ammonium*, and its compounds with alcohol-radicles constitute the class of bodies called urethanes: *e.g.* carbamate of ethyl or ethyl-urethane, $C^3H^7NO^2 = \left.\begin{matrix} NH^2(CO)'' \\ C^2H^5 \end{matrix}\right\} O$. These bodies might also be regarded empirically as compounds of carbonic anhydride with the corresponding alcohol-bases: *e.g.* ethylurethane as $CO^2 + C^2H^7N$ (ethylamine); but their formation and properties do not accord with this latter view.

The urethanes are produced, together with sal-ammoniac, by the action of ammonia gas on the chlorocarbonates of the alcohol-radicles:

$$\underset{\text{Chlorocarbonate of ethyl.}}{C^2H^5.CO^2Cl} + 2NH^3 = NH^4Cl + \underset{\text{Ethyl-urethane.}}{C^2H^5.CH^2NO^2}$$

2. By the action of anhydrous ammonia on the corresponding carbonic ethers:



$$\underset{\text{Carbonate ethyl.}}{\left.\begin{matrix} (CO)'' \\ (C^2H^5)^2 \end{matrix}\right\} O} + NH^3 = \underset{\text{Carbamate of ethyl.}}{\left.\begin{matrix} NH^2(CO)'' \\ C^2H^5 \end{matrix}\right\} O} + \underset{\text{Alcohol.}}{C^2H^5.H.O.}$$

3. By the action of chloride of cyanogen on the alcohols:

$$C^2H^5.H.O + CN.Cl + H^2O = \left.\begin{matrix} NH^2(CO)'' \\ C^2H^5 \end{matrix}\right\} O + HCl$$

Carbamic acid in which the whole of the oxygen is replaced by sulphur, constitutes sulphocarbamic acid, CH^3NS^2 (*q. v.*)

There is also an oxysulphocarbamic acid, the ethyl- and amyl-salts of which have been obtained, viz. xanthamide, $\left.\begin{matrix} NH^2(CO)'' \\ C^2H^5 \end{matrix}\right\} S$, and xanthamylamide $\left.\begin{matrix} NH^2(CO)'' \\ C^5H^{11} \end{matrix}\right\} S$. (See those articles; also page 206.)

Carbamate of Ammonium. *Anhydrous Carbonate of Ammonia.* $N^2H^6CO^2 = \left.\begin{matrix} NH^2(CO)'' \\ NH^4 \end{matrix}\right\} O$.— This salt, which was discovered by H. Davy, and further investigated by J. Davy and H. Rose, is produced: 1. By passing a mixture of carbonic anhydride and ammonia-gas through a number of glass tubes cooled to a low temperature. In whatever proportion the gases may be mixed, they always unite in the proportion of 2 vol. NH^3 to 1 vol. CO^2.—2. By subliming a mixture of carbonate of sodium and sulphamate of ammonium, $N^2H^6SO^3$, both perfectly dry. (H. Rose.)

It is a white mass which smells of ammonia, has a strong alkaline reaction, volatilises a little above 60° C., and condenses again below 60°. The specific gravity of its vapour is 0·8992 (H. Rose), 0·90 (Bineau). Now 2 vols. ammonia + 1 vol. CO^2, weigh $1·1787 + 1·5252 = 2·7039$, which is nearly three times the observed specific gravity of the vapour. Hence the two gases appear to unite without condensation, although not in equal volumes. Probably the compound exists only in the solid state, and is resolved by heat into CO^2 and $2NH^3$.

Vapour of sulphuric anhydride converts carbamate of ammonium into sulphamate of ammonium with evolution of carbonic anhydride. Heated in sulphurous anhydride, it yields an orange-coloured sublimate. Hydrochloric acid decomposes it with aid of heat, yielding sal-ammoniac and carbonic anhydride.

Carbamate of ammonium dissolves readily in water, yielding a solution which gives the reactions of neutral carbonate of ammonium, from which, indeed, it differs only by the elements of water $[N^2H^6CO^2 = (N^2H^4)^2CO^3 - H^2O]$. It appears, however to be capable of existing in solution for a short time as carbamate; for on passing carbonic anhydride into aqueous ammonia, taking care that the liquid does not become hot, the resulting solution does not precipitate chloride of calcium or chloride of barium till after some time, unless the liquid be heated. This circumstance is of importance in chemical analysis; thus, in determining the amount of carbonic acid in a mineral water by means of chloride of calcium and ammonia, it is necessary to leave the liquid to stand for some time, or heat it to the boiling point, in order to insure that the whole of the carbonic acid is precipitated as carbonate of calcium. (Kolbe.)

According to H. Rose, ordinary carbonate of ammonium prepared by sublimation often contains carbamate. (Gm. ii. 430).

Carbamate of Amyl. *Amyl-urethane*, $C^6H^{13}NO^2 = CH^2(C^5H^{11})NO^2$.—(Medlock, Ann. Ch. Pharm. lxxi. 104.—A. Wurtz, J. Pharm. [3] xx. 22).—Obtained by adding ammonia to amylic alcohol saturated with chlorocarbonic oxide, and washing the resulting crystalline mass with water to separate sal-ammoniac; or by passing gaseous chloride of cyanogen into amylic alcohol and distilling, chloride of amyl then passing over first, and afterwards the carbamate.

This compound crystallises from boiling water in beautiful silky needles, soluble in alcohol and ether. It melts at 66° C. and distils without alteration at 220°. Distilled with caustic baryta, it yields ammonia and amylic alcohol, with a residue of carbonate of barium. It dissolves completely in cold sulphuric acid, and is precipitated therefrom by water. Heated with sulphuric acid, it forms amyl-sulphuric acid and ammonia, with evolution of carbonic and sulphurous anhydrides.

Carbamate of Ethyl. *Urethane.* $C^3H^7NO^2 = CH^2(C^2H^5)NO^2$. (Dumas. Ann. Ch. Phys. liv. 233.– Cahours, Compt. rend. xxi. 629.—Liebig and Wöhler, Ann. Ch. Pharm. liv. 370.—Gerhardt, Compt. chim. 1846, p. 120.—Wurtz, Compt. rend. xxii. 503, J. Pharm. [3] xx. 19) —This compound is prepared: 1. By leaving carbonate of ethyl in contact with an equal volume of aqueous ammonia in a corked flask till it completely disappears, and evaporating in a dry vacuum.—2. By treating chlorocarbonate of ethyl with ammonia, and distilling: the action is very violent.—Alcohol of ordinary strength is saturated with gaseous chloride of cyanogen; the solution is heated for some hours in a sealed long-necked flask placed in a water-bath; and the liquid when cold is decanted from the deposit of sal-ammoniac arising from a secondary action, and distilled. Chloride of ethyl then passes over first, then alcohol at 80° C.

(p. 749), after which, the temperature rises, and urethane passes over, condensing in laminæ.

Carbamate of ethyl forms large transparent colourless crystals: even a few drops of its solution left to evaporate are sure to yield these crystals. It melts below 100° C., and distils at about 180° without alteration if dry; but in the moist state it suffers partial decomposition, giving off torrents of ammonia. It dissolves readily in water, forming a solution which does not precipitate silver-salts; also in alcohol and ether. Its vapour-density, by experiment, is 3·14, by calculation (2 vols.) = 3·08.

Carbamate of Methyl. *Urethylane.* $C^2H^5NO^2 = CH^2(CH^3)NO^2$.—Obtained like the preceding compounds. Crystallises in long tables derived from an oblique rhomboïdal prism, with very elongated terminal faces. The crystals are not deliquescent, they melt between 52° and 55° C., and solidify at 52° when perfectly dry. Boiling-point 177° C. Vapour-density, experimental = 2·62; by calculation (2 vol.) = 2·60. It is very soluble in water, less in alcohol, and still less in ether. 100 pts. of water at 11° C. dissolve 217 pts. of it, whereas 100 pts. alcohol at 15° C. dissolve only 73 pts. Dilute sulphuric acid decomposes urethylane into methylic alcohol, acid sulphate of ammonium, and carbonic anhydride:

$$\left.\begin{matrix}NH^2(CO)''\\CH^3\end{matrix}\right\}O + \left.\begin{matrix}SO^2\\H^2\end{matrix}\right\}O^2 + H^2O = CH^3.H.O + \left.\begin{matrix}SO^2\\H.NH^4\end{matrix}\right\}O^2 + CO^2.$$

Strong sulphuric acid blackens it, eliminating sulphurous anhydride and inflammable gases. Potash decomposes it in the same manner as dilute sulphuric acid.

Carbamate of Tetryl. $C^5H^{11}NO^2 = CH^2(C^4H^9)NO^2$.—Obtained by heating tetrylic alcoholic with liquid chloride of cyanogen, best in a sealed tube, distilling and collecting that which passes over above 220° C. This distillate solidifies on cooling in a crystalline mass, which, when recrystallised from boiling alcohol, forms shining nacreous scales, unctuous to the touch, insoluble in water, soluble in alcohol and ether; they melt at a gentle heat and distil without alteration. (Humann, Ann. Ch. Phys. [3] xliv. 340.)

Substitution-derivatives of Carbamic Acid.

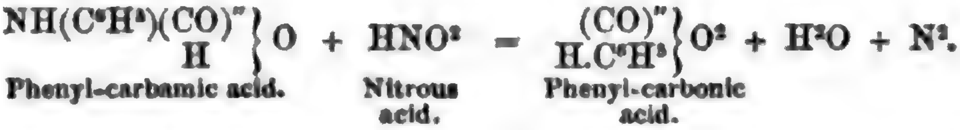
Ethyl-carbamic Acid. $C^3H^7NO^2 = \left.\begin{matrix}NH(C^2H^5)(CO)''\\H\end{matrix}\right\}O$.—This acid, isomeric with urethane, is not known in the free state; but its ethylammonium-salt, $\left.\begin{matrix}NH(C^2H^5)(CO)''\\C^2H^8N\end{matrix}\right\}O$, is identical with the so-called *anhydrous carbonate of ethylamine*, $(C^2H^7N)^2.CO^2$, obtained by passing carbonic anhydride into anhydrous ethylamine cooled by a freezing mixture. It is a snow-white powder, whose aqueous solution, like that of carbamate of ammonium, does not immediately precipitate chloride of barium, unless aided by heat. (Wurtz, Ann. Ch. Phys. [3] xxx. 483.)

Ethylcarbamate of Ethyl. Ethylurethane. $C^5H^{11}NO^2 = C^3H^6(C^2H^5)NO^2$.—Produced by heating cyanate of ethyl with alcohol in a sealed tube: $C(C^2H^5)NO + C^2H^6O = C^5H^{11}NO^2$; sometimes obtained as an accessory product in the preparation of cyanate of ethyl. It is an oily liquid, smelling like carbonate of ethyl. Specific gravity 0·9862. Boiling point 174—175° C. Vapour-density 4·071. Potash decomposes it, forming alcohol, ethylamine, and carbonate of potassium: $C^5H^{11}NO^2 + 2KHO = C^2H^6O + C^2H^7N + K^2CO^3$. Heated with strong sulphuric acid, it yields carbonic anhydride, sulphate of ethylamine, and probably also ethylsulphuric acid. (Wurtz, Compt. rend. xxxvii. 182; Gerh. ii. 929; iv. 869.)

Methyl-carbamic Acid, like the corresponding ethyl-compound, is not known in the separate state, but forms a methylammonium-salt, $\left.\begin{matrix}NH(CH^3)(CO)''\\CH^6N\end{matrix}\right\}O$, which may also be regarded as *anhydrous carbonate of methylamine*, $(CH^5N)^2.CO^2$: it is formed by passing carbonic anhydride into dry methylamine, or by distilling a mixture of fused hydrochlorate of methylamine and carbonate of calcium. In the latter case, however, it is mixed with carbonate of methylamine. (Wurtz, Ann. Ch. Phys [3] xxx. 450, 461.)

Phenyl-carbamic Acid. *Carbanilic Acid. Anthranilic Acid.* $C^7H^7NO^2 = \left.\begin{matrix}NH(C^6H^5)(CO)''\\H\end{matrix}\right\}O$. (Fritzsche, Ann. Ch. Pharm. xxxix. 83; Liebig, *ibid.* xxxix. 91; Gerland, Chem. Soc. Qu. J. v. 133.)—This acid, which contains the elements of 1 at. carbonic anhydride and 1 at. phenylamine, C^6H^7N, and is likewise isomeric with oxybenzamic acid, is obtained by boiling indigo with strong caustic potash, replacing the water as it evaporates, and adding peroxide of manganese before the indigo completely disappears, till the liquid no longer deposits blue indigo on being left at rest. The mass is then dissolved in water and supersaturated with dilute sulphuric acid; the filtered liquid is neutralised with potash and evaporated to dryness; and the residue is digested with alcohol, which dissolves chiefly phenyl-carbamate of potassium, and leaves it in an impure state when evaporated. It is then dissolved in water, acetic acid added, and the yellow or brownish crystals of phenyl-carbamic acid thereby precipitated are purified by animal charcoal and recrystallisation (Fritzsche). According to Chancel this acid is likewise produced by the action of potash on phenyl-carbamide.

Phenyl-carbamic acid crystallises in transparent, colourless, shining prisms or laminæ, often of considerable size. It dissolves very sparingly in cold water, much more in boiling water, very easily in alcohol and ether. Its solutions have an acid reaction. It melts at 132° C., and sublimes unaltered. By distillation from coarsely pounded glass, it is resolved into carbonic anhydride and phenylamine. It carbonises when heated with phosphoric anhydride. Strong sulphuric acid converts it into phenyl-sulphamic acid. When nitrous acid gas is passed into its warm dilute aqueous solution nitrogen is evolved, and the solution yields, when concentrated, crystals of salicylic (phenyl-carbonic acid):



$$\underset{\text{Phenyl-carbamic acid.}}{\left.\begin{matrix}NH(C^6H^5)(CO)''\\H\end{matrix}\right\}O} + \underset{\substack{\text{Nitrous}\\\text{acid.}}}{HNO^2} = \underset{\substack{\text{Phenyl-carbonic}\\\text{acid.}}}{\left.\begin{matrix}(CO)''\\H.C^6H^4\end{matrix}\right\}O^2} + H^2O + N^2.$$

The metallic phenyl-carbamates are but little known. The *calcium-salt*, $C^7H^6CaNO^2$, forms rhombohedral crystals, sparingly soluble in cold, moderately in boiling water. The *silver-salt*, $C^7H^6AgNO^2$, is deposited in shining laminæ on mixing a dilute boiling solution of the calcium-salt with nitrate of silver. The solution of the ammonium-salt likewise precipitates the salts of *copper*, *lead*, and *zinc*.

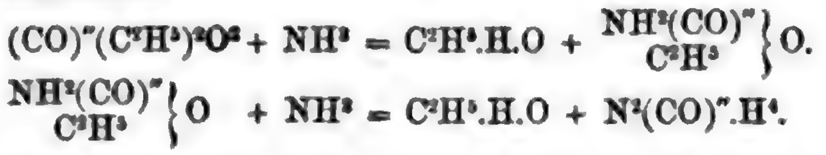
Phenyl-carbamates (?) *of Ethyl and Methyl.*—Chancel (Compt. rend. xxx. 751), by treating the nitrobenzoates of ethyl and methyl with sulphydrate of ammonium, obtained compound ethers, which he regards as phenyl-carbamates; but from their mode of formation it is more probable that they are oxybenzamates, which are isomeric therewith. (See OXYBENZAMIC ACID.)

CARBAMIDE. $CH^4N^2O = N^2.(CO)''.H^2.H^2$.—This compound is the primary diamide of carbonic acid, and has the same composition as urea, with which indeed it is in all probability identical. It is formed in various ways:

1. By the action of ammonia on oxychloride of carbon, both being perfectly dry (Regnault, Ann. Ch. Phys. [2] lxix. 180; Natanson, Ann. Ch. Pharm. xcviii. 287):

$$COCl^2 + 4NH^3 = CH^4N^2O + 2NH^4Cl.$$

The mixture of carbamide and sal-ammoniac thus produced is soluble in water and in aqueous alcohol; and on adding excess of baryta-water to the solution, evaporating in vacuo, exhausting the residue with absolute alcohol, evaporating to dryness, dissolving in a small quantity of water, treating the solution with nitric acid, and decomposing the resulting nitrate of carbamide with carbonate of barium, the carbamide is obtained in the separate state (Natanson).—2. By the action of ammonia on carbonate of ethyl. When the two substances are heated together in a sealed tube to 180° C., carbamate of ethyl is first formed (at 100°), and afterwards converted by the excess of ammonia into carbamide:



$$(CO)''(C^2H^5)^2O^2 + NH^3 = C^2H^5.H.O + \left.\begin{matrix}NH^2(CO)''\\C^2H^5\end{matrix}\right\}O.$$

$$\left.\begin{matrix}NH^2(CO)''\\C^2H^5\end{matrix}\right\}O + NH^3 = C^2H^5.H.O + N^2(CO)''.H^4.$$

3. By the action of heat on the isomeric compound, cyanate of ammonium, $NH^4.CNO$, or even when a solution of that salt is left to evaporate spontaneously, also when cyanate of potassium is mixed with sulphate of ammonium, the mixture left to evaporate, and the residue exhausted with alcohol.—4. By decomposing ammonio-cupric fulminate with sulphydric acid (see FULMINIC ACID).—5. In the decomposition of oxamide (*q. v.*) at a red heat.—6. By the oxidation of uric acid.

The product obtained by the last four processes is urea; the same substance occurs as an animal excretion in the urine, in which indeed it was first discovered, being produced by the oxidation of the nitrogenous tissues. Whether the carbamide produced by the action of ammonia on carbonic ether or on oxychloride of carbon is identical with this, or only isomeric, is a point perhaps not absolutely decided. Nevertheless it agrees with urea in its most essential characters, viz. in forming a sparingly soluble crystalline salt with nitric acid, and in being resolved by the action of the stronger acids into ammonia and carbonic anhydride, as represented by the equation:

$$CH^4N^2O + H^2O = 2NH^3 + CO^2.$$

It is true that Regnault did not obtain a crystalline salt by adding nitric acid to the mixture of carbamide and sal-ammoniac produced by the first process; perhaps in consequence of the presence of the sal-ammoniac. Natanson, however, did obtain a crystalline nitrate in the manner above described. No decided difference has, indeed, been pointed out between carbamide and urea. We shall, however, refer to the article Urea for the preparation and properties of the substance usually so called, and shall here describe a number of substitution-products, commonly called *compound ureas.*

Substitution-products of Carbamide: Compound Ureas.

The hydrogen in carbamide may be more or less replaced by organic radicles, acid or basic. The compounds containing 1 at. of an alcohol-radicle, are obtained chiefly by the action of ammonia on the cyanates of those radicles, just as carbamide or urea itself is produced by the action of ammonia on cyanic acid (cyanate of hydrogen.)

$$\underset{\text{Cyanic Acid.}}{HCNO} + NH^3 = \underset{\text{Carbamide.}}{CH^4N^2O.}$$

$$\underset{\text{Cyanate of Ethyl.}}{C^2H^5.CNO} + NH^3 = \underset{\text{Ethyl-carbamide.}}{CH^3(C^2H^5)N^2O.}$$

Those which contain 2 at. of an alcohol-radicle are produced in like manner by the action of an amine-base on the cyanate of an alcohol-radicle, *e.g.* ethyl-allylcarbamide, by the action of ethylamine on cyanate of allyl. All these carbamides containing basic radicles form crystalline-salts with nitric acid, and are resolved by the action of sulphuric or hydrochloric acid, or of alkalis, into carbonic anhydride and an amine base, just as carbamide is resolved under similar circumstances into carbonic anhydride and ammonia.

The carbamides containing acid radicles are produced by the action of the chlorides of those radicles on urea. They do not form salts with nitric acid. When heated they are resolved into cyanuric acid and the corresponding acid amide (*vide infra*).

a. Carbamides or *Ureas containing Acid radicles.* (Zinin, Ann. Ch. Pharm. xcii. 403.—Moldenhauer, *ibid.* xciv. 100.)

Acetyl-carbamide. $C^3H^6N^2O^2 = N^2\left\{\begin{matrix}(CO)''\\ C^2H^3O.\\ H^3\end{matrix}\right.$ Crystallises from boiling alcohol in long silky needles, and from boiling water, in stars or tufts of rhomboïdal prisms Dissolves in 100 pts. of cold and 10 pts. of boiling alcohol; much more soluble in water, insoluble in ether. At 160° C. it yields a slight woolly sublimate; melts at 200° (Zinin), at 112° (Moldenhauer), and at a higher temperature is resolved into cyanuric acid and acetamide:

$$3C^3H^6N^2O^2 = C^3H^3N^3O^3 + 3(N.H^2.C^7H^3O).$$

It is not precipitated by nitric acid or by mercuric nitrate.

Benzoyl-carbamide. $C^8H^8N^2O^2 = N^2.(CO)''.C^7H^5O.H^3$.—Obtained by heating powdered urea with chloride of benzoyl to 150°—155° C. As soon as all the urea is melted upon the chloride, the mixture must be removed from the bath and briskly stirred, whereupon it becomes pasty. The product washed with cold alcohol yields benzoyl-carbamide as a crystalline powder. It crystallises from boiling alcohol in thin elongated rectangular laminæ, often united in groups. It is much less soluble in water and in ether than in cold alcohol; strong boiling hydrochloric acid dissolves it better than pure water. Heated on platinum-foil it melts, emitting the odour of cyanide of phenyl (benzonitrile), afterwards that of cyanic acid, and finally volatilises altogether. Heated to 200° C. in a tube, it melts to a colourless liquid, which at a higher temperature, is resolved into cyanuric acid and benzamide. Ammonia has no action on benzoyl-carbamide. Potash dissolves it readily, and acids separate it from the solution. The alkaline solution, when boiled, gives off ammonia, and forms carbonate and benzoate of the alkali-metal.

Butyryl-carbamide, $C^5H^{10}N^2O^2 = N^2.(CO)''.C^4H^7O.H^3$.—Crystallises readily from water in small scales, from alcohol in thin elongated rhombic laminæ. It is tasteless and inodorous. Melts at 176° C. to a yellowish liquid which solidifies in a crystalline mass on cooling. A high temperature decomposes it like acetyl-urea. It aqueous solution is not precipitated by nitric acid, oxalic acid, or mercuric nitrate.

Valeryl-carbamide, $C^6H^{12}N^2O^2 = N^2(CO)''.C^5H^9O.H^3$, crystallises from boiling water in small nacreous crystals, unctuous to the touch; from alcohol in needles. It is nearly insoluble in cold water, melts at 91° C. and when carefully heated yields a sublimate of large iridescent scales.

β. Carbamides or *Ureas containing Basylous radicles:*

Allyl-carbamide, $C^4H^8N^2O = N^2.(CO)^{\prime\prime}.C^3H^5.H^3$. (Cahours and Hofmann, Phil. Trans. 1855, p. 555.)—Obtained by the action of ammonia on cyanate of allyl, ($C^3H^5.CNO + NH^3 = C^4H^8N^2O$.) Crystallises easily by evaporation both from water and from alcohol. Its composition is that of thiosinamine in which the sulphur is replaced by oxygen.

Allyl-sulphocarbamide, $N^2.(CS)^{\prime\prime}.C^3H^5.H^3$, also called thiosinamine, is produced by the action of ammonia on oil of mustard. Ethyl-, phenyl-, and naphthyl-derivatives of it are produced by treating oil of mustard with ethylamine, phenylamine and naphthylamine.

Diallyl-carbamide. *Sinapoline.* $C^7H^{12}N^2O = N^2.(CO)^{\prime\prime}.(C^3H^5)^2.H^2$. — Produced: 1. By the action of oxide of lead and water on sulphocyanate of allyl (oil of mustard):

$$2(C^3H^5.CNS) + 3Pb^2O + H^2O = C^7H^{12}N^2O + Pb^2CO^3 + 2Pb^2S.$$

2. By heating cyanate of allyl with water or with aqueous potash:

$$2(C^3H^5.CNO) + H^2O = C^7H^{12}N^2O + CO^2.$$

If potash is used, care must be taken that the action does not go too far; otherwise nothing but amine-bases will be formed (Cahours and Hofmann. *loc. cit.*) For the properties and reactions of this compound, see Sinapoline.

Amyl-carbamide. $C^6H^{14}N^2O = N^2.(CO)^{\prime\prime}.C^5H^{11}.H^3$. (A. Wurtz, Compt. rend. xxxii. 417).—Produced by the action of ammonia on cyanate of amyl. It is decomposed by potash into amylamine and carbonate of potassium. It forms a crystalline nitrate.

Benzyl-carbamide. *Toluyl-urea.* $C^8H^{10}N^2O = N^2.(CO)^{\prime\prime}.C^7H^7.H^3$.—This substance, or more probably an isomer thereof, is produced by the action of sulphydrate of ammonium on nitrotoluamide. (Noad, Phil. Mag. [4] vii. 142. (See Toluamide.)

Ethyl-carbamide, $C^3H^8N^2O = N^2.(CO)^{\prime\prime}.C^2H^5.H^3$. (Wurtz, Compt. rend. xxxii. 414.)—Produced by the action of ammonia on cyanate of ethyl. Dissolves readily in water and alcohol, and crystallises from alcohol in large prisms which decompose at 200° C., with evolution of ammonia and other products. The aqueous solution is decomposed by chlorine, forming a heavy liquid which crystallises gradually. Nitric acid does not form a precipitate in the aqueous solution, but crystals of nitrate of ethyl-carbamide are obtained on evaporation.

Diethyl-carbamide, $C^5H^{12}N^2O = N^2.(CO)^{\prime\prime}.(C^2H^5)^2.H^2$.—Produced, like the allyl-compound, by the action of water on cyanate of ethyl; also by the action of ethylamine on cyanate of ethyl: $C^2H^5.CNO + C^2H^7N = C^5H^{12}N^2O$. The nitrate forms very acid deliquescent rhombic prisms containing $C^5H^{12}N^2O.HNO^3$. (Wurtz.)

Ethyl-allyl-carbamide, $C^6H^{12}N^2O = N^2.(CO)^{\prime\prime}.C^2H^5.C^3H^5.H^2$. (Cahours and Hofmann, *loc. cit.*)—By the action of ethylamine on cyanide of allyl. Crystallises in beautiful prisms.

Similar compounds are formed by the action of methylamine, amylamine, and phenylamine on cyanate of allyl.

Ethyl-allyl-sulphocarbamide, $N^2(CS)^{\prime\prime}.C^2H^5.C^3H^5.H^2$. Syn. of Ethylthiosinamine. (See Thiosinamine.)

Ethyl-amyl-carbamide, $C^8H^{18}N^2O = N^2(CO)^{\prime\prime}.C^2H^5.C^5H^{11}.H^2$. — Action of amylamine on cyanate of ethyl. (Wurtz.)

Methyl-carbamide, $C^2H^6N^2O = N^2.(CO)^{\prime\prime}.CH^3.H^3$. (Wurtz, *loc. cit.*)—Obtained by the action of ammonia on cyanate of methyl; also by evaporating a mixture of sulphate of methylamine and cyanate of potassium and extracting the residue with alcohol. Crystallises in long transparent deliquescent prisms. The aqueous solution is neutral to test-paper, and if somewhat concentrated yields with nitric acid a precipitate of $C^2H^6N^2O.HNO^3$.

Dimethyl-carbamide, $C^3H^8N^2O = N^2.(CO)^{\prime\prime}.(CH^3)^2.H^2$. (Wurtz, *loc. cit.*)—Isomeric with ethyl-carbamide. Produced by the action of water, or of methylamine on cyanate of methyl. Crystallises easily; melts at 97° C.; is permanent in the air; volatilises without alteration; dissolves readily in water and alcohol; combines with nitric acid, forming the salt $C^3H^8N^2O.HNO^3$.

Methyl-ethyl-carbamide. $C^4H^{10}N^2O = N^2.(CO)^{\prime\prime}.CH^3.C^2H^5.H^2$.—Very deliquescent substance, obtained by the action of methylamine on cyanate of ethyl. (Wurtz.)

Naphthyl-carbamide, $C^{11}H^{10}N^2O = N^2(CO^{\prime\prime}).C^{10}H^7.H^3$. (H. Schiff, Chem. Gaz. 1857, p. 211.)—Obtained by saturating a solution of naphthylamine in anhydrous ether with cyanic acid gas, and recrystallising from hot alcohol. Flat, shining, flexible needles, nearly insoluble in water, more soluble in alcohol, easily soluble in ether: the latter solution yields a crystalline precipitate with oxalic acid. Naphthyl-carbamide yields by spontaneous decomposition, a resinous substance, whose alcoholic solution is coloured violet by acids, and red again by alkalis. The same reaction has been observed to be produced on test-paper by a tincture of madder (Sacc), and by nitrosonaphthalin (Church and Perkin, Jahresber. d. Chem. 1856, p. 609).

NAPHTHYL-ALLYL-SULPHOCARBAMIDE. $N^2(CS'').C^{10}H^7.C^3H^5.H^2$.—Syn. of NAPHTHYL-THIOSINAMINE. (See THIOSINAMINE.)

PHENYL-CARBAMIDE, $C^7H^8N^2O = N^2.(CO)''.C^6H^5.H^3$. *Phenyl-urea, Aniline-urea, Carbanilamide, Carbamide-carbanilide.* (A. W. Hofmann, Ann. Ch. Pharm. liii. 57; lvii. 265; lxx. 130; lxxiv. 14; Gm. xi. 503.)—This compound is obtained: 1. By passing cyanic acid vapour into anhydrous phenylamine, kept as cool as possible; dissolving the resulting crystalline mass in hot water; filtering to separate diphenyl-carbamide (which is produced more abundantly in proportion as the phenylamine has been more heated); and cooling the filtrate to the crystallising point.—2. By treating sulphate or hydrochlorate of phenylamine with aqueous cyanate of potassium, and separating the resulting phenyl-carbamide (cyanate of phenylamine) by digestion in alcohol.—3. By mixing phenylamine with an aqueous solution of chloride of cyanogen (obtained by passing chlorine gas through aqueous hydrocyanic acid), purifying the resulting crystals with animal charcoal, and recrystallising from hot water.—4. Cyanate of phenyl mixed with ammonia, immediately solidifies in the form of phenyl-carbamide, $C^6H^5.CNO + NH^3 = C^7H^8N^2O$.

Phenyl-carbamide forms fusible needles and laminæ, sparingly soluble in cold, easily in boiling *water*, easily also in *alcohol* and *ether*. It dissolves in *nitric acid*, but scarcely to a greater amount than in water, and crystallises therefrom unaltered, differing in this respect from carbamide. It dissolves also without alteration in *cold sulphuric acid*, but when heated therewith, it is resolved into carbonic anhydride,, phenyl-sulphamic acid, and acid sulphate of ammonium:

$$C^7H^8N^2O + 2H^2SO^4 = CO^2 + \left.\begin{matrix} N.H.C^6H^5.(SO^2)'' \\ H \end{matrix}\right\} O + NH^4.H.SO^4.$$

Heated above its melting-point, it is resolved into ammonia, diphenyl-carbamide, and cyanuric acid:

$$\underset{\text{Phenyl-carbamide.}}{6[N^2.(CO)''.C^6H^5.H^3]} = 3NH^3 + \underset{\text{Diphenyl-carbamide.}}{3[N^2.(CO)''.(C^6H^5)^2.H^2]} + \underset{\text{Cyanuric acid.}}{N^3.H^3.(\overset{'''}{CO})^3}$$

By boiling with strong *potash-ley*, or more quickly by fusion with *hydrate of potassium*, it yields ammonia, phenylamine, and carbonate of potassium:

$$C^7H^8N^2O + 2KHO = NH^3 + C^6H^7N + K^2CO^3.$$

It is not decomposed by boiling with dilute acids or alkalis.

The name *phenyl-urea* has hitherto been generally applied to the isomeric compound, which Chancel obtained by the action of sulphydrate of ammonium on nitrobenzamide (Gerh. Traité, i. 427). This compound is a powerful base; but it does not agree with the ureas, either in its mode of formation, or in its reaction with alkalis. It should rather be regarded as *oxybenzodiamide* (*q. v.*) the primary diamide of oxybenzoic acid ($C^7H^6O^3$). Its formation may be represented by the equation:

$$\underset{\text{Nitrobenzamide.}}{N\left\{\begin{matrix} C^7H^4(NO^2)O \\ H^2 \end{matrix}\right.} + 3H^2S = \underset{\text{Oxybenzo-diamide.}}{N^2\left\{\begin{matrix} (C^7H^4O)'' \\ H^4 \end{matrix}\right.} + 2H^2O + S^3.$$

When treated with potash, it yields ammonia, and an acid which is probably oxybenzoic acid. The reaction consists of two stages, ammonia and oxybenzamic acid being formed in the first, ammonia and oxybenzoic acid in the second:

$$\underset{\text{Oxybenzo-diamide.}}{N^2\left\{\begin{matrix} (C^7H^4O)'' \\ H^4 \end{matrix}\right.} + H^2O = NH^3 + \underset{\text{Oxybenzamic acid.}}{\left.\begin{matrix} N.H^2.(C^7H^4O)'' \\ H \end{matrix}\right\} O}$$

$$\underset{\text{Oxybenzamic acid.}}{\left.\begin{matrix} N.H^2.(C^7H^4O)'' \\ H \end{matrix}\right\} O} + H^2O = NH^3 + \underset{\text{Oxybenzoic acid.*}}{\left.\begin{matrix} C^7H^4O \\ H^2 \end{matrix}\right\} O^2}$$

The true phenyl-urea is the compound above described as phenyl-carbamide.

ETHYL-PHENYL-CARBAMIDE, $C^9H^{12}N^2O = N^2.(CO)''.C^2H^5.C^6H^5.H^2$, is obtained by dissolving phenylamine in cyanate of ethyl. Great heat is evolved, and the mixture on cooling solidifies to a crystalline mass. It is slowly decomposed by potash, yielding phenylamine, ethylamine, and carbonic anhydride. (Wurtz, Compt. rend. xxxii. 417.)

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[*] See a paper by Dr. Hofmann (Proc. Roy. Soc. x. 602), where however the acid formed is said to be not oxybenzoic, but benzoic acid.

NITROPHENYL-CARBAMIDE, $C^7H^7N^3O^3 = N^2.(CO)''.C^6H^4(NO^2).H^3$. — Produced, together with dinitromelaniline, by the action of gaseous chloride of cyanogen on nitrophenylamine dissolved in ether. (Hofmann, Ann. Ch. Pharm. lxvii. 156; lxx. 137.)

DIPHENYL-CARBAMIDE. *Diphenyl-urea, Carbanilide, Carbophenylamide.* $C^{13}H^{12}N^2O = N^2.(CO)''.(C^6H^5)^2.H^2$ (Hofmann, Ann. Ch. Pharm. lvii. 266; Gm. xi. 349).—Produced: 1. By the action of cyanate of phenyl on phenylamine, or on water:

$$2[N.(CO)''.C^6H^5] + H^2O = CO^2 + N^2.(CO)''.(C^6H^5)^2.H^2.$$

2. By the action of phenylamine on oxychloride of carbon.—3. In the decomposition of diphenyl-sulphocarbamide by potash.—4. By the dry distillation of phenyl-carbamide, melanoximide, or oxalate of melaniline. (See those compounds.)

Diphenyl-carbamide forms white silky needles, which melt at 205° C. and distil without decomposition. It is odourless at ordinary temperatures, but has a suffocating odour when heated. It dissolves sparingly in *water*, abundantly in *alcohol* and *ether*.

When quickly heated in the moist state, it yields carbonate of phenylamine, together with other products. With strong *sulphuric acid*, it gives off carbonic anhydride, and forms water and phenylsulphamic acid:

$$N^2\left\{\begin{matrix}(CO)''\\(C^6H^5)^2\\H^2\end{matrix}\right. + 2\left(\begin{matrix}SO^2\\H^2\end{matrix}\right\}O^2\Big) = (CO)''.O + H^2O + 2\left(\begin{matrix}N.H.C^6H^4.(SO^2)''\\H\end{matrix}\right\}O.\Big)$$

By boiling with *potash*, it is resolved into phenylamine and carbonate of potassium.

Diphenyl-carbamide is isomeric with *flavine*, an organic base produced by the action of reducing agents on dinitrobenzophenone. This base is indeed sometimes regarded as diphenyl-urea (Gerh. i. 430); but it does not exhibit the characters of a urea. (See FLAVINE.)

PHENYLSULPHOCARBAMIDE, $C^7H^8N^2S = N^2(CS)''.C^6H^5.H^3$. (Hofmann, Proceedings of the Royal Society, ix. 276.)—Produced by the action of alcoholic ammonia on sulphocyanate of phenyl:

$$C^6H^5.CNS + NH^3 = C^7H^8N^2S.$$

The mixture, on being gently warmed, quickly solidifies into a crystalline compound, which may be obtained in beautiful needles by crystallisation from boiling water.

Phenylsulphocarbamide is a weak base, and forms a *chloroplatinate* containing $C^7H^8N^2S.HCl.PtCl^2$. It also combines with *nitrate of silver*. By boiling with nitrate of silver, it is converted into phenyl-carbamide.

PHENYL-ALLYL-SULPHOCARBAMIDE. $N^2.(CS)''.C^6H^5.C^3H^5.H^2$. — Syn. with PHENYL-THIOSINAMINE. (See THIOSINAMINE.)

DIPHENYL-SULPHOCARBAMIDE. *Sulphocarbanilide, Sulphophenyl-urea.* $C^{13}H^{12}N^2S = N^2(CS)''.(C^6H^5)^2.H^2$. (Hofmann, Ann. Ch. Pharm. lvii. 266; lxx. 144; Gm. xi. 350. Further, Proc. Roy. Soc. x. 274.—Laurent and Delbos, J. Pharm. [3] x. 309.—Laurent and Gerhardt, Ann. Ch. Phys. [3] xxii. 103; xxiv. 196.)—This compound is obtained: 1. By the action of sulphide of carbon on phenylamine, the action being accelerated by addition of alcohol (Hofmann):

$$2C^6H^7N + CS^2 = C^{13}H^{12}N^2S + H^2S.$$

—2. By heating a mixture of phenylamine, sulphocyanate of potassium, and sulphuric acid, the diphenyl-sulphocarbamide then distilling over, while sulphate of ammonium remains behind (Laurent and Gerhardt).—3. By mixing phenylamine with sulphocyanate of phenyl: $C^6H^5.CNS + C^6H^7N = C^{13}H^{12}N^2S$. (Hofmann.)

Diphenyl-sulphocarbamide separates from the mixture of phenylamine and sulphide of carbon, in crystalline scales or rhombic tables; from alcohol, in brilliant iridescent laminæ. It dissolves sparingly in water, easily in alcohol. It has a peculiar odour, especially when heated, and a bitter taste exceeding in intensity that of any other known substance. It melts at 140° C., and distils without decomposition. Heated with strong *sulphuric acid*, it forms phenyl-sulphamic acid, giving off carbonic anhydride and sulphydric acid (Hofmann):

$$C^{13}H^{12}N^2S + 2H^2SO^4 = CO^2 + H^2S + 2\left(\begin{matrix}N.H.C^6H^4.(SO^2)''\\H\end{matrix}\right\}O\Big)$$

By *phosphoric anhydride*, *chloride of zinc*, or *hydrochloric acid gas*, it is resolved into phenylamine and sulphocyanate of phenyl (Hofmann). Fused with *potash*, it yields phenylamine, together with sulphydrate and carbonate of potassium:

$$C^{13}H^{12}N^2S + 3KHO = 2C^6H^7N + K^2CO^3 + KHS.$$

When boiled with *alcoholic potash*, it is converted into diphenyl-carbamide:

$$C^{13}H^{12}N^2S + K^2O = K^2S + C^{13}H^{12}N^2O.$$

Similarly when its alcoholic solution is boiled with *mercuric oxide*. It is not decomposed by dilute acids or alkalis.

PIPERYL-CARBAMIDE. *Piperyl-urea, Piperidine-urea.* $C^6H^{12}N^2O = N^2(CO)''.C^5H^{10}.H^2$ (Cahours, Ann. Ch. Phys. [3] xxxviii. 76.)—Obtained by boiling sulphate of piperidine with cyanate of potassium, evaporating to dryness, and exhausting with strong alcohol. It appears also to be formed when vapour of cyanic acid or moist chloride of cyanogen is passed into piperidine. The alcoholic solution yields it, by spontaneous evaporation, in long white needles.

Methyl-piperyl-carbamide, $C^6H^{11}(CH^3)N^2O$, and *Ethyl-piperyl-carbamide*, $C^6H^{11}(C^2H^5)N^2O$, are produced by the action of piperidine on the cyanates of methyl and ethyl.

CARBANIL. Syn. of CYANATE OF PHENYL. (See CYANIC ETHERS.)

CARBANILIDE. Syn. of DIPHENYL-CARBAMIDE (p. 756).

CARBANILIC ACID. Syn. of PHENYL-CARBAMIC ACID (p. 751).

CARBANILETHANE and **CARBANIMETHYLANE.** PHENYLCARBAMATES OF ETHYL and METHYL (p. 752).

CARBAZOTE. The name given by Thaulow (J. pr. Chem. xxxi. 220) to the gas evolved by ignition of cyanide of silver, which he regards as isomeric but not identical with cyanogen. It has a peculiar odour, and strongly irritates the eyes and respiratory organs. Specific gravity 1·73. Liquefies at $-4°$ C. Burns with red flame. It dissolves in potash, and the solution when neutralised with nitric acid does not precipitate iron-salts. (Thaulow.)

CARBAZOTIC ACID. Syn. with PICRIC ACID.

CARBIDES, or *Carburets*. Compounds of carbon with metals. These compounds have not been much studied: none of them occur as natural minerals, and it is difficult to obtain them in definite form. The usual effect of the union of carbon with a metal, is to render it hard and brittle. (See the several metals.)

CARBOBENZIDE. Syn. with BENZONE.

CARBOBENZOIC ACID. See CINNAMEIN (p. 981).

CARBO-HYDROGENS. See HYDROCARBONS.

CARBOLIC ACID. Syn. with PHENIC ACID.

CARBON. *Symbol* C. *Atomic weight* 12.—Carbon is one of the most abundant of the elements, existing both in the free state and in an endless variety of combinations. It is found pure in the diamond; nearly pure in graphite or plumbago, less pure as anthracite. It occurs also abundantly in the form of carbonates, especially carbonate of calcium, and is an essential constituent of organic bodies, from which it may be separated in the form of charcoal, by distilling off the more volatile elements, hydrogen, oxygen, nitrogen, &c.

Carbon in the free state is a solid body, destitute of taste and odour, infusible and non-volatile, excepting at the temperature produced by a powerful electric current. The several modifications exhibit great diversities of colour, lustre, transparency, hardness, density, and power of conducting heat and electricity. It exhibits crystalline forms belonging to two different systems, the regular and the hexagonal, and several amorphous modifications.

1. *Diamond.* This valuable gem consists of pure or nearly pure carbon. It is found in alluvial soils produced by the disintegration of ancient rocks, the principal localities being in India, Borneo, Brazil, and the Urals. Diamonds occur thinly scattered through large quantities of soil, and very careful washing and examination are required to separate them.

The diamond crystallises in forms belonging to the regular system, namely, the octahedron, which is usually the predominating form, though it rarely occurs alone; also the cube, the rhomboïdal dodecahedron, which is very frequent; the triakis-octahedron, a figure of 24 faces, formed by the superposition of a low triangular pyramid on each face of the octahedron; and the hexakis-octahedron, a 48-sided figure formed in like manner, by a 6-faced acumination of the octahedron. Intermediate forms are also of frequent occurrence, the secondary faces being sometimes so numerous as to give the crystal the appearance of having convex faces. Sometimes the faces are really curved, and consequently intersect in curved edges: the dodecahedron and octahedron frequently occur with convex faces. Hemihedral forms and twin-crystals are also found. (For figures, see the article CRYSTALLOGRAPHY.)

All diamonds cleave easily in directions parallel to other faces of the regular octahedron, which is therefore the primary form. The fracture is conchoïdal. The specific gravity of the diamond is 3·5295 according to Thomson; 3·55 according to Pelouze. It is the hardest substance known, being capable of scratching all others. Diamonds with curved edges are also capable of cutting glass, and are much used for that purpose, the curved edges penetrating the glass like a wedge; those with straight edges merely scratch.

The purest diamonds are colourless and transparent; but many exhibit various shades of yellow, red, green, brown, and black; these coloured diamonds leave, when burnt, from 0·65 to 0·2 per cent. of ash: colourless diamonds leave but a trace. The diamond has a strong lustre (called *adamantine*), and high refractive and dispersive power: hence its peculiar brilliancy. The lustre of the natural diamond is greatly increased by cutting it in a peculiar manner, so as to give it numerous facets capable of reflecting and dispersing light in various directions. This is effected by pressing the diamond against a revolving metal disc covered with a mixture of diamond dust and oil, no other substance being hard enough to abrade the diamond. The dust for this purpose is obtained either by collecting that which falls away in the process of cutting and polishing, or by pounding up diamonds which have not sufficient transparency to be valuable as gems. Diamonds are sometimes found in opaque spheroïdal lumps, destitute of crystalline structure and transparency, and useless excepting in the form of powder.

The diamond conducts electricity but slowly. Like all other forms of carbon, it neither melts nor volatilises at the heat of the most powerful furnace; but when placed between the charcoal cones of a powerful voltaic battery, it becomes white-hot, swells up, splits into fragments, and after cooling, presents the aspect of coke prepared from bituminous coal. When very strongly heated in the air or in oxygen gas, it takes fire and burns completely away, forming carbonic anhydride. This fact of the combustibility of the diamond, which had been conjectured by Newton from its great refracting power, was first demonstrated in 1694, by the Florentine academicians, who succeeded in burning it in the focus of a concave mirror. Lavoisier and Guyton-Morveau, and afterwards Davy, showed that the sole product of the combustion in oxygen is carbonic anhydride, and therefore that the diamond is pure carbon.

2. *Graphite.*—This name is applied to several varieties of native carbon containing from 95 to nearly 100 per cent. of that element, some crystalline, others amorphous, but all perfectly opaque, having an iron-black or steel-grey colour, and metallic lustre, producing a black shining streak on paper; sectile; of specific gravity 1·209, hardness between 1 and 2, and conducting electricity nearly as well as the metals. Graphite was formerly regarded as a carbide of iron, but the iron is now known to be merely in a state of mixture, as also small quantities of silica and alumina.

α. *Crystallised or Foliated Graphite.*—This variety is found occasionally in small six-sided tables belonging to the hexagonal system, cleaving perfectly in the direction of the base, and having the basal planes striated parallel to the alternate sides. More commonly, however, it occurs in foliated or granular masses. It is found imbedded in quartz near Travancore in Ceylon, and near Moreton Bay in Australia; with olivine and sphene at Ticonderoga in the State of New York, and in gneiss at Stourbridge, Massachussets, where it presents a structure between scaly and fine granular, and an occasional approximation to distinct crystallisations (Dana, ii. 27). It is also obtained artificially by melting cast-iron containing a large proportion of carbon and leaving it to cool slowly. It is tough and difficult to pulverise by mechanical means, but it may be reduced to the state of very thin laminæ by prolonged trituration with water.

β. *Amorphous Graphite.*—This variety, also called *plumbago* or *black lead*, is found in Borrowdale, Cumberland, where it occurs in nests of trap in the clay-slate, and is largely imported into this country from Germany, principally from Griesbach near Passau. The Borrowdale mine was formerly very rich, but now appears to be nearly exhausted (see *Ure's Dictionary of Arts, Manufactures and Mines*, iii. 467). Amorphous graphite is softer than the crystalline variety, and makes a much blacker streak on paper: it is therefore better adapted for the making of pencils. Some kinds of amorphous graphite, occurring in the coal measures, have very much the appearance of anthracite: such is the case with the graphite of New Brunswick.

Graphite resembles the other modifications of carbon in being unalterable when heated in close vessels, excepting at the temperature of the electric current, and in yielding carbonic anhydride when burnt in contact with oxygen. But it differs essentially from all other forms of carbon when subjected to the action of certain oxidising agents, such as a mixture of chlorate or acid chromate of potassium with sulphuric or nitric acid, or a mixture of nitric and sulphuric acids. In this case Brodie has shown (Ann. Ch. Phys. [3] xlvi. 351; further, Phil. Trans. 1860, i.; Ann. Ch. Pharm. cxiv. 7) that it is converted into a peculiar acid, called *graphitic acid*, which is best obtained by heating pulverised graphite with chlorate of potassium and nitric acid, as long as yellow vapours are given off, then washing it with a large quantity of water, drying it on the water-bath, and repeating this series of operations several times. In this manner the graphite is ultimately converted into thin transparent crystals of graphitic acid, $C^{11}H^4O^5$. Brodie, however, regards this acid as analogous in composition to the acid $Si^4H^4O^5$, which Wöhler obtained by the action of oxidising agents on graphitoïdal silicon; and accordingly he supposes that the atomic weight of graphite is different from that of the other forms of carbon, and equal to 33, which he denotes by the symbol Gr (graphon); substituting this value in the preceding formula of graphitic acid, it becomes $Gr^4H^4O^5$. (See ATOMIC WEIGHT OF CARBON, p. 757; also GRAPHITIC ACID.)

Graphite cannot be converted into graphitic acid by a single treatment with oxidising agents, however long continued; but by subjecting it to this treatment for a certain time, then washing it with water and igniting, it may be purified and obtained in a state of very minute division. A good way of proceeding is to mix coarsely pounded graphite with $\frac{1}{14}$ of its weight of chlorate of potassium, add the mixture to a quantity of strong sulphuric acid equal to twice the weight of the graphite, heat the whole in the water-bath as long as yellow vapours of chloric oxide are evolved, wash the cooled mass with water, then dry and ignite it; it then swells up and leaves finely divided graphite. If the graphite to be purified contains siliceous matters, a little fluoride of sodium should be added to the mixture before heating.

Graphite is used for making pencils, for polishing stoves, and other articles, for diminishing the friction of machinery, for making crucibles, and in the electrotype process for coating the surfaces of wood and other non-conducting materials, so as to render them conductive.

3. *Anthracite* or *stone-coal* is an amorphous variety of carbon containing about 90 per cent. of that element associated with hydrogen, oxygen, nitrogen, and ash. It is intermediate in composition and properties between graphite and bituminous coal, being blacker than graphite, and having a higher lustre than ordinary coal. Specific gravity 1·3 to 1·7. Hardness = 2 to 2·1. It burns with difficulty, requiring a strong draught to keep it in a state of active combustion: hence it is fit only for burning in close stoves and furnaces; it does not cake together like bituminous coal. Anthracite occurs abundantly in South Wales, in the departments of Mayenne and Isère in France; also in Pennsylvania and Rhode Island.

4. *Carbon obtained from Organic Substances by Dry Distillation or Imperfect Combustion.*—When animal or vegetable substances are strongly heated in close vessels, the more volatile elements, viz. the oxygen, hydrogen, and nitrogen, with part of the carbon, are driven off in the form of gaseous products, some of which afterwards condense in the liquid form, while a considerable portion of the carbon remains behind in the form of a black mass, called charcoal, of greater or less compactness, according to the nature of the original substance. If the substance thus treated — wood or coal, for example — contains any inorganic materials, such as potash, soda, lime, &c., these remain behind with the charcoal. The purest kind of charcoal is that obtained by heating sugar, starch, or some other organic substance, free from inorganic elements, in a close vessel. There then remains a black, brilliant, porous charcoal, which is nearly pure carbon, but contains a small quantity of hydrogen and oxygen, which cannot be driven off even by the most intense and long-continued heat.

a. Wood-Charcoal.—Wood consists of carbon, hydrogen, and oxygen, the two latter being in the proportion to form water. When heated in the open air, it burns completely away, with the exception of a small quantity of white ash; but if the supply of air is limited, only the more volatile ingredients burn away, and the greater part of the carbon remains behind. This is the principle of the process of *charcoal-burning* as it is practised in countries where wood is abundant, on the Harz mountains in Germany, for instance. A number of billets of wood are built up vertically in two or three rows into a large conical heap, which is covered over with turf or moistened charcoal-ash, holes being left at the bottom for the air to get in. A hollow space is also left in the middle of the heap, to serve as a flue for the gaseous matters which are evolved. The heap is set on fire by throwing burning pieces of wood into the central opening, near the top of which, however, a kind of grate, made of billets of wood, is placed, to prevent the burning fuel from falling at once to the bottom. The combustion then proceeds gradually from the top to the bottom, and from the centre to the outside of the heap; and as the central portions burn away, fresh wood is continually thrown in at the top, so as to keep the heap quite full. The appearance of the smoke shows how the combustion is proceeding; when it is going on properly, the smoke is thick and white; if it becomes thin, and especially if a blue flame appears, it is a sign that the wood is burning away too fast, and the combustion must then be checked by partially stopping up the holes at the bottom, or by heaping fresh ashes on the top and sides, and pressing them down well so as to diminish the draught. As soon as the combustion is completed, the heap is completely covered with turf or ashes, and left to cool for two or three days. It is then taken to pieces, and the portions still hot are cooled by throwing water or sand upon them. The quantity of charcoal thus obtained varies with the manner in which the combustion is conducted. 100 parts of wood yield on the average from 61 to 65 parts by measure, or 24 parts by weight of charcoal. When the burning is very carefully conducted, the quantity may amount to 70 per cent. by measure.

In England a large quantity of charcoal is obtained in the dry distillation of wood for the preparation of acetic acid. For this purpose the wood is heated to redness in cast-iron cylinders, whereupon a number of volatile products are given off, including a large quantity of tarry matter, an inflammable spirit called wood-spirit or wood-naphtha, and acetic acid; and in the retorts there remains a quantity of charcoal.

For the manufacture of gunpowder, charcoal is sometimes prepared by subjecting wood in iron cylinders to the action of over-heated steam. (Violette, Ann. Ch. Phys. [3] xxiii. 475.)

Wood-charcoal is more or less compact, according to the kind of wood from which it is formed. The lighter woods, such as willow, yield a very porous charcoal, having comparatively little power of conducting heat and electricity; box-wood, on the contrary, yields a very compact charcoal, which is a good conductor of heat and electricity, and is admirably adapted for exhibiting the voltaic light. The density and conducting power of charcoal are greatly increased by exposing it in close vessels to a very high temperature. Charcoal retains the form, and to a considerable extent the external structure of the wood, so that a horizontal section exhibits distinctly the concentric rings and the traces of the medullary rays. When burned it leaves from 1 to 5 per cent. of ash. According to Berthier, 1000 parts of lime-wood leave 50 parts of ash; of oak, 25; birch 10; fir 8; hornbeam 26; beech 30.

b. Coke.—Ordinary bituminous coal, which consists of the remains of ancient forests and peat-mosses, and appears to have been formed from wood by a process of slow decay going on without access of air, differs from wood in containing a larger proportion of carbon, and less oxygen and hydrogen; it also contains nitrogen derived from the tissue of the plants. This substance, when heated in the open air, burns away like wood, leaving nothing but a white ash; but, when strongly heated in cast-iron cylinders, it undergoes a decomposition like that which takes place in wood under similar circumstances, a large quantity of volatile products being given off, viz. carburetted hydrogen gas (the gas used for illumination) and a tarry liquid containing ammonia and a variety of other products; while a black, dull-looking, porous mass, called *coke*, is left in the retorts. This substance also consists mainly of carbon, mixed, however, with a quantity of inorganic constituents, greater than that which occurs in wood-charcoal, so that it leaves a larger amount of ash when burned. The aspect of coke varies greatly according to the kind of coal from which it is obtained. Bituminous coals, such as the Newcastle coal, undergo a kind of semi-fusion before they decompose, and yield a very porous coke, having a brilliant metallic aspect; anthracite, on the contrary undergoes but little alteration by heating, and yields a coke having very much of the form and aspect of the original mass. Coke is used in the iron districts of South Wales and Staffordshire, for reducing the metal from the ore. It is there prepared from the coal which occurs in the same districts, by partially burning that substance in longitudinal heaps, more or less covered up with the ashes of former fires, the object being to produce a smothered combustion, similar to that already described as used for the preparation of wood-charcoal. This process is very wasteful unless carefully conducted.

c. Metallic Carbon, Glance-coal.—This is a very dense form of carbon, deposited when certain volatile organic compounds, especially hydrocarbons, are passed through red-hot tubes of porcelain or cast-iron; it collects in the upper part of the retorts in which carburetted hydrogen gas is distilled from coal, and is likewise produced in blast furnaces. It often exhibits the lustre and sonority of a metal, is very hard, a good conductor of heat and electricity, and burns with difficulty. It is used to form the negative element in Bunsen's voltaic battery.

A very hard and compact carbon, also used for the purpose just mentioned, is obtained by heating to redness, in an iron mould, an intimate and impalpable mixture of 2 pts. coke and 1 pt. bituminous coal, then several times steeping it in treacle, and subjecting it again to a very intense heat. The mass thus formed is very hard, may be sawn and filed without breaking, and conducts electricity like a metal.

d. Lamp-black.—Most of our ordinary combustibles, consisting of carbon and hydrogen, such as tallow, wax, and oil, undergo but imperfect combustion, unless assisted by an artificial draught of air. The consequence is, that a portion of the carbon, which is the less combustible element of the two, remains unburned, and is driven off in smoke, or deposited on cold surfaces in the form of *soot* or *lamp-black;* thus, a plate of glass or metal held in the upper part of a candle flame is quickly covered with a black deposit of carbon. Lamp-black is ordinarily prepared by the imperfect combustion of highly carbonised bodies, such as resin or pitch. The apparatus consists of a cylindrical stone chamber, in which is suspended a cone of iron plate, having a hole at top, and capable of moving up and down; this cone serves for a chimney during the operation. A cast-iron pot, containing the resin or pitch, is heated in a furnace outside the chamber; the vapours proceeding from it are set on fire; and the supply of air is properly regulated by apertures which may be opened and closed at pleasure. The imperfect combustion of the vapour produces a considerable quantity of lamp-black, which collects on the cone and on the walls. When the operation is finished, the cone is lowered, and as it is made to fit the chamber exactly, it scrapes the wall as it descends, and causes the deposit to fall down on the floor. Lamp-black thus obtained is always contaminated with oily matter; it may be purified by calcination in a covered crucible. Sometimes the chamber is hung with coarse cloths, on which the soot collects; they are withdrawn from time to time and scraped.

A better method of condensation is to cause the smoke and vapour to pass through an inclined iron tube, in which the oily products collect, and thence into a series of condensing chambers; the purest product is then found in the farthest chamber. The finest kind of lamp-black is obtained by burning oil or fat in lamps, and causing the products of combustion to pass through a series of iron cylinders, terminating in a chimney; the cylinders are opened at bottom from time to time, and the carbonaceous deposit removed. As obtained by either of these methods it is always more or less contaminated with oily matter. It may be purified by calcination in a covered crucible, but for the purposes to which it is chiefly applied, viz. for painting and for the manufacture of printing ink, the presence of the oil is not objectionable.

e. Animal Charcoal or *Bone-black*, is a mixture of very finely divided charcoal and phosphate of calcium obtained by calcining bones in close vessels. Its preparation and properties have been already described (p. 624).

Absorbent power of Charcoal.—Wood-charcoal and other porous forms of carbon have the property of absorbing large quantities of gases: the greater the porosity of the charcoal the greater is also its absorbing power. In its ordinary state, however, charcoal has its pores filled with atmospheric air, and to enable it to exert its full absorbing power on any other gas, it must first be freed from the air contained in it by heating it to redness and cooling it under mercury. Saussure has shown that recently ignited box-wood charcoal absorbs at 12° C. and under a pressure of 724 millimetres, the following quantities of different gases:

Ammonia . . .	90 vols.	Ethylene . .	35 vols.
Hydrochloric acid .	85 „	Carbonic oxide .	9·42 „
Sulphurous anhydride	65 „	Oxygen . . .	9·25 „
Sulphydric acid . .	55 „	Nitrogen . .	6·50 „
Nitrous oxide . .	40 „	Hydrogen . .	1·25 „
Carbonic anhydride .	35 „		

Charcoal also absorbs moisture with avidity from the air, as well as other condensable vapours, such as odoriferous effluvia. Hence freshly calcined charcoal, wrapped up in clothes which have acquired a disagreeable colour, destroys that odour. It has a considerable effect in retarding the putrefaction of animal matter with which it is placed in contact. Water is found to remain sweet, and wine to be improved in quality, if kept in casks the inside of which has been charred. In the state of coarse powder, wood-charcoal is particularly applicable as a filter for spirits, which it deprives of the essential oil they contain. (Graham's *Elements of Chemistry*, 2nd ed. vol. i. p. 338.) Water contaminated with offensive gas and other matters may also be rendered fit for drinking by filtering it through coarsely pounded charcoal interposed between two layers of sand.

Charcoal not only absorbs gases, but frequently also determines their combination. If a piece of charcoal, which has remained for some time in an atmosphere of sulphuretted hydrogen, and has absorbed a considerable quantity of that gas, be introduced into a vessel filled with oxygen, combination immediately takes place between the oxygen and the elements of the sulphuretted hydrogen, water and sulphurous acid being formed, and a portion of the sulphur separated. The charcoal always becomes very hot, and sometimes the heat is great enough to produce explosion. Similar phenomena are exhibited by other combustible gases.

This property of charcoal has been applied by Dr. Stenhouse to the construction of ventilators and respirators for purifying infected atmospheres. In a pamphlet, bearing the title "On Charcoal as a Disinfectant," Dr. Stenhouse observes: — "Charcoal not only absorbs effluvia and gaseous bodies, but, especially, when in contact with atmospheric air, rapidly oxidises and destroys many of the easily alterable ones, by resolving them into the simplest combinations they are capable of forming, which are chiefly water and carbonic acid. . . . Effluvia and miasmata are generally regarded as highly organised, nitrogenous, easily alterable bodies. When these are absorbed by charcoal, they come in contact with highly condensed oxygen gas, which exists within the pores of all charcoal which has been exposed to the air, even for a few minutes; in this way they are oxidised and destroyed." On this principle, Dr. Stenhouse has constructed *ventilators*, consisting of a layer of charcoal enclosed between two sheets of wire-gauze, to purify the foul air which accumulates in water-closets, the wards of hospitals, and in the back courts and lanes of large cities. By the use of these ventilators, pure air may be obtained from exceedingly impure sources, the impurities being absorbed and retained by the charcoal, while a current of pure air alone is admitted into the neighbouring apartments. A similar contrivance might also be applied to the gulley-holes of our common sewers, and to the sinks in private houses. Dr. Stenhouse has also constructed *respirators*, consisting of a layer of charcoal a quarter of an inch thick, interposed between two sheets of silvered wire-gauze covered with woollen cloth. They are made either to cover the mouth and nose, or the mouth alone; the former kind of respirator affords an effectual protection against malaria and the deleterious gases which accumulate in chemical works, common sewers, &c. The latter will answer the same purpose when the atmosphere is not very impure, provided the simple precaution be taken of inspiring the air by the mouth, and expiring by the nose. This form of respirator may also be useful to persons affected with fetid breath. Freshly heated wood-charcoal simply placed in a thin layer in trays, and disposed about infected apartments, such as the wards of hospitals, is also highly efficacious in absorbing the noxious matter.

Platinised Charcoal.—The power of charcoal in inducing chemical combination is increased by combination with minutely divided platinum. In this manner, a combination may be produced possessing the absorbent power of charcoal (which is much greater than that of spongy platinum), and nearly equal, as a promoter of chemical combination, to spongy platinum itself. In order to platinise charcoal, nothing more is necessary than to boil it, either in coarse powder or in large pieces, in a solution of dichloride of platinum, and, when thoroughly impregnated, which seldom requires more than ten minutes or a quarter of an hour, to heat it to redness in a closed vessel, a capacious platinum crucible being well adapted for the purpose. Charcoal thus platinised, and containing 3 grains of platinum to 50 grains of charcoal, causes oxygen and hydrogen gases to unite completely in a few minutes; with a larger proportion of platinum, the gases combine with explosive violence, just as if platinum-black were used. Cold platinised charcoal, held in a jet of hydrogen, speedily becomes incandescent, and inflames the gas. Platinised charcoal slightly warmed rapidly becomes incandescent in a current of coal gas, but does not inflame the gas, owing to the very high temperature required for that purpose. In the vapour of alcohol or wood-spirit, platinised charcoal becomes red-hot, and continues so till the supply of vapour is exhausted. Spirit of wine, in contact with platinised charcoal and air, is converted in a few hours into vinegar. Two per cent. of platinum is sufficient to platinise charcoal for most purposes. Charcoal containing this amount of platinum, causes oxygen and hydrogen to combine perfectly in about a quarter of an hour, and such is the strength of platinised charcoal which seems best adapted for disinfectant respirators. Charcoal containing only 1 per cent. of platinum causes oxygen and hydrogen to combine in about two hours; and charcoal containing the extremely small amount of $\frac{1}{4}$ per cent. of platinum, produces the same effect in six or eight hours. Platinised charcoal seems likely to admit of various useful applications; one of the most obvious of these is its adaptability to air-filters and respirators. From its powerful oxidising properties, it might also prove a highly useful application to malignant ulcers and similar sores, on which it will act as a mild but effective caustic. It might also be found useful in Bunsen's carbon battery. (Stenhouse, Chem. Soc. Qu. J. viii. 105.)

Charcoal as a Precipitant and Decoloriser.—Wood-charcoal and animal charcoal, especially the latter, possess the power of forming insoluble compounds with many dissolved substances, more particularly organic colouring matters. It precipitates iodine from its solution in iodide of potassium, also lime, nitrate of lead, and most metallic sub-salts, from their aqueous solutions: it likewise separates metallic acids from their solutions in alkalis. A solution of acetate or nitrate of lead, in which charcoal is immersed, is found after a while to contain free acetic or nitric acid. A large number of organic substances, besides colouring matters, are likewise precipitated by charcoal, viz. the bitter principles of the hop, gentian, and aloes, tannin, organic alkaloids; also resins from solution in alcohol. It is important to bear this in mind in analysing liquids which have been decolorised by animal charcoal, as many of the substances originally contained in the solution may have been carried down by the charcoal.

The peculiar power of bone-black in removing colouring matters, &c. from solution, is due to the more minute division of the charcoal resulting from the interposition of the earthy matter. If this be dissolved out by an acid, the decolorising power of the charcoal is greatly impaired, which however must be done for certain applications of it, as in the preparation of vegetable acids. Charcoal of much higher decolorising power than bone-black, is obtained by calcining dried blood, horns, hoofs, clippings of hides, glue, and other animal matters, in contact with pearl-ash, and washing the calcined mass with water. A charcoal of considerable decolorising power may likewise be prepared by carbonising vegetable substances mixed with chalk, calcined flints, or any other earthy matter. If 100 pts. of pipe-clay, made into a thin paste with water, be well mixed with 20 pts. of tan and 500 pts. of finely pounded coal, and the mass dried and ignited in a close vessel, a charcoal will be obtained very little inferior in decolorising power to bone-black. The following table, taken from Graham's *Elements of Chemistry*, 2nd edition, vol. i. p. 361, shows the efficiency of different kinds of charcoal in removing colouring matter. These substances are compared with bone-black, as being the most feeble species. The relative efficiency is not the same for different kinds of colouring matter.

Species of Charcoal. (same weight).	Relative decoloration of sulphate of indigo.	Relative decoloration of syrups.
Blood charred with pearlash . . .	50	20
Blood charred with chalk . . .	18	11
Blood charred with phosphate of calcium .	12	10
Glue charred with pearlash . . .	36	15·5
White of egg charred with the same .	34	15·5
Gluten charred with the same . . .	10·6	8·8
Charcoal from acetate of potassium . .	5·6	4·4
Charcoal from acetate of sodium . .	12	8·8
Lamp-black not calcined	4	3·3
Lamp-black calcined with pearlash . .	15·2	10·6
Bone-charcoal, after the extraction of the earth of bones by an acid, and calcination with potash	45	20
Bone-charcoal, treated with an acid . .	1·87	1·6
Oil charred with phosphate of calcium .	2	1·9
Bone-charcoal in its ordinary state . .	1	1

[On the preparation, properties, and uses of the various forms of carbon, see further. *Ure's Dictionary of Arts, Manufactures and Mines*, articles Bone-Black, Charcoal, Coke, and Lamp-Black.—Pelouze et Frémy, *Traité de Chimie*, 3me éd. i. 705—821.]

Compounds of Carbon.—Carbon unites with most other elements, but generally speaking not directly, most of its compounds being formed either in the bodies of living plants and animals in a way which we cannot trace, or derived by substitution from such compounds. The only elements with which it unites directly are oxygen, sulphur, nitrogen, and a few metals, and with these only at high temperatures. For *oxygen*, carbon exhibits no affinity at ordinary temperatures, but at a red heat, it not only combines readily with free oxygen, but is capable of separating that element from its combinations with all others, even from potassium. The temperature required for determining the combination depends upon the density of the carbon: porous wood charcoal begins to burn in the air at about 240° C.; the more compact kinds require a higher temperature; anthracite and graphite still higher; and the diamond the highest of all. The product of the combustion is carbonic anhydride, CO^2, mixed, however, if the supply of oxygen is deficient, with the lower oxide CO.

With *sulphur*, carbon also unites at a red heat, forming disulphide of carbon, CS^2.—With *nitrogen*, it unites at a red heat, provided an alkali be present, forming cyanogen, CN, which enters into combination with the alkali-metal; thus, when nitrogen gas is passed over ignited charcoal saturated with carbonate of potassium, cyanide of potassium is formed.—With *metals* also, carbon appears to unite directly under certain circumstances, as in the formation of steel by keeping iron imbedded in charcoal powder at a white heat.

The compounds of carbon and *hydrogen* constitute a very important group of organic bodies, many of them, as oil of turpentine, $C^{10}H^{16}$, existing ready formed in plants, while others, as ethylene, C^2H^4, and naphthalene, $C^{10}H^8$, are produced by the decomposition of more complex organic compounds. Most of them play the part of radicles, being capable of combining, like metals, with chlorine, oxygen, sulphur, &c., of replacing hydrogen in combination, and passing as entire groups from one state of combination to another: *e.g. ethyl*, C^2H^5, *amyl*, C^5H^{11}, *allyl*, C^3H^5, *ethylene*, C^2H^4, *amylene*, C^5H^{10}, &c. The hydrogen in these hydrocarbons, may be more or less replaced by chlorine, bromine, nitryl (NO^2), and other elements or groups, whereby derivative radicles are formed, also capable of entering into combination, replacing hydrogen, &c. like simple radicles, *e. g. bromethyl*, C^2H^4Br, *chlorethylene*, C^2H^3Cl, *dinitronaphthalene*, $C^{10}H^6(NO^2)^2$, &c. When the hydrogen in a hydrocarbon is thus completely replaced by another element, a chloride, bromide, &c. of carbon is produced. In this manner, tetrachloride of carbon CCl^4, is formed from marsh-gas CH^4, dichloride of carbon, C^2Cl^4, from ethylene, C^2H^4, &c.

CARBON, BROMIDES OF. Several of these compounds appear to exist, but only one of them, the *dibromide* C^2Br^4, has been analysed.* This body is obtained by treating alcohol or ether with bromine, saturating the resulting hydrobromic acid with potash, distilling, and treating the residue with water. Dibromide of carbon then remains as a white crystalline deposit which may be purified by washing with water (Löwig, Ann. Ch. Pharm. iii. 292). Its formation is represented by the equations:

$$\underset{\text{Alcohol.}}{C^2H^6O} + 4Br^2 = C^2Br^4 + 4HBr + H^2O.$$

$$\underset{\text{Ether.}}{C^4H^{10}O} + 8Br^2 = 2C^2Br^4 + 8HBr + H^2O.$$

It is also produced by the action of alcoholic potash on the dibromide of tribromethylene (Lennox, Chem. Soc. Qu. J. xiv. 209):

$$C^2HBr^3.Br^2 + KHO = C^2Br^4 + KBr + H^2O.$$

Dibromide of carbon forms white crystalline plates, unctuous to the touch, having an ethereal odour and saccharine taste; it melts at 50° C., and sublimes without alteration. It is nearly insoluble in water, very soluble in alcohol and ether; not decomposed by acids or alkalis. It burns in the flame of a spirit lamp, giving off vapours of hydrobromic acid, but ceases to burn as soon as it is removed from the flame. Chlorine attacks it in the melted state, forming chloride of bromine. Heated with oxide of mercury or passed over red-hot oxide of zinc, copper, or iron, it yields metallic bromine and carbonic anhydride. When passed over red-hot metallic zinc, copper, or iron, it also yields a bromide of the metal without disengagement of gas. (Lowig.)

Commercial bromine sometimes contains a liquid bromide of carbon, which may also be obtained by the action of bromine on ether and alcohol, especially if chlorine is likewise present. It is an oily, colourless, fragrant liquid of specific gravity 2·436, not solidifiable at − 25° C., boiling at 120° C., so that it is easily separated from bromine by distillation. It is insoluble in water, not decomposed by acids or dilute alkalis, but decomposed by fusion with hydrate of potassium, into bromide and carbonate of potassium (Poselger, Ann. Ch. Pharm. lxiv. 287). The same compound appears to be produced by the action of 2 pts. bromine on 1 pt. iodide of ethylene, $C^2H^4I^2$, and may be separated from bromide of iodine by means of dilute potash.

In the preparation of bromine, there is sometimes formed an oily ethereal liquid called *oil of bromine*, which appears to contain $C^2H^2Br^4$. When dropped on red-hot fragments of glass, it yields a deposit of carbon, together with crystals and a dark-brown oil, while hydrobromic acid and a combustible gas escape. The dark-brown oil appears to be a portion of the liquid which has remained undecomposed and has absorbed bromine, and the crystals consist of a bromide of carbon C^4Br^2. (M. Hermann, Ann. Ch. Pharm. xcv. 211.)

CARBON, CHLORIDES OF. Carbon does not unite directly with chlorine: but several compounds of these elements are obtained by the action of chlorine, aided by light or heat, on organic bodies, chiefly on hydrocarbons or their chlorinated derivatives, *e. g.* CCl^4 from marsh-gas (CH^4), or chloroform ($CHCl^3$), C^2Cl^4 from ethylene (C^2H^4), C^3Cl^6 from tritylene (C^3H^6), $C^{10}Cl^8$ from naphthalene ($C^{10}H^8$), &c. It is customary, however, to restrict the term chloride of carbon to four of these bodies, containing 1 and 2 atoms of carbon, while the rest are regarded as substitution-derivatives of organic radicles, *e. g.* $C^{10}Cl^8$, as perchloronaphthalene. The names and formulæ of these four compounds are given in the following table, in the left-hand column, according to the atomic weight of carbon [12] here adopted, in the right-hand column according to the smaller atomic weight of carbon [6], the latter being the names by which they are generally known:

[C = 12]			[*C* = 6]	
Protochloride . .	C^2Cl^2	or	Subchloride . .	C^4Cl^2
Dichloride . . .	C^2Cl^4	„	Protochloride . .	C^4Cl^4
Trichloride . . .	C^2Cl^6	„	Sesquichloride .	C^4Cl^6
Tetrachloride . .	CCl^4	„	Di- or Bi-chloride .	C^2Cl^4

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* C^2Br^6 has been recently obtained. See ETHYLENES, BROMINATED.

There is, however, no real distinction between these four compounds and others formed of the same two elements, excepting that they are of lower atomic weight, and that they may be derived from disulphide of carbon, the vapour of that substance mixed with chlorine and passed through a hot tube yielding the tetrachloride, and the other three being produced, either by exposing this compound to a higher temperature or by the action of reducing agents.

TETRACHLORIDE OF CARBON, CCl^4. *Dichloride or Bichloride of Carbon. Carbonic chloride. Perchlorinated Chloride of Methyl. Perchloroformene.*—This compound, which is an analogue of marsh-gas CH^4, and of carbonic anhydride CO^2, was discovered by Regnault in 1839 (Ann. Ch. Phys. [2] lxxi. 337). It is produced: 1. By the action of chlorine on marsh-gas (Dumas, Ann. Ch. Phys. [3] lxxiii. 95).—2. By the action of chlorine on chloroform in sunshine: $CHCl^3 + Cl^2 = HCl + CCl^4$. Chloroform is gently heated in a retort exposed to the sun, and a stream of dry chlorine is passed slowly and continuously through it, the liquid which distils over being repeatedly poured back till hydrochloric acid ceases to be evolved, after which the distillate is agitated with mercury to remove free chlorine, and then rectified (Regnault).—3. By the action of chlorine on disulphide of carbon: $CS^2 + 4Cl^2 = CCl^4 + 2SCl^2$. Chlorine saturated with vapour of sulphide of carbon by passing through the liquid is made to pass through a red-hot tube containing fragments of porcelain and connected with a receiver surrounded with ice; and the yellowish-red mixture of tetrachloride of carbon and chloride of sulphur thereby obtained is very slowly added to an excess of potash-ley or milk of lime, the mixture being agitated from time to time and afterwards distilled. Tetrachloride of carbon then passes over, sometimes mixed with sulphide of carbon, if too much of that compound was mixed with the chlorine, or if the heat was not strong enough; the sulphide of carbon may be removed by leaving the liquid for some time in contact with potash-ley (Kolbe, Ann. Ch. Pharm. xlv. 41; liv. 146). Geuther (*ibid.* cvii. 212) removes the sulphide of carbon, by dissolving the mixture in alcohol, adding alcoholic potash as long as it thereby acquires a darker colour, and heating the liquid gently to promote the conversion of the sulphide of carbon into xanthate of potassium; then separates the unaltered chloride of carbon by water; and purifies it by washing.—4. By the action of pentachloride of antimony on disulphide of carbon:

$$CS^2 + 2SbCl^5 = CCl^4 + 2SbCl^3 + S^2.$$

The mixture becomes hot, and on cooling deposits crystals of trichloride of antimony mixed with sulphur, while tetrachloride of carbon remains in the liquid state. (Hofmann, Chem. Soc. Qu. J. xiii. 65.)

Properties.—Tetrachloride of carbon is a thin transparent colourless oil, having a pungent aromatic odour. Specific gravity 1·56. Boiling point 77° C. Vapour-density by experiment 5·24—5·33, representing a condensation to 2 vols. $\left(\frac{12 + 4 \,.\, 35{\cdot}5}{2} \times 0{\cdot}0693 = 5{\cdot}34.\right)$ It is insoluble in water, but soluble in alcohol and in ether.

Decompositions.—Tetrachloride of carbon passed through a red-hot tube, is resolved into free chlorine and a lower chloride of carbon, which, at a bright red heat is chiefly C^2Cl^4, at a still higher temperature C^2Cl^2, and at a dull red heat, a body isomeric with C^2Cl^6, but having only half the vapour-density of that compound (Regnault).—2. When mixed with *hydrogen* and passed through a red-hot tube filled with pumice, it yields marsh-gas and ethylene (Berthelot, Ann. Ch. Phys. liii. 69; Jahresber. d. Chem. 1858, p. 519).—3. With *sulphuretted hydrogen*, in like manner, at a low red heat it yields hydrochloric acid and sulphochloride of carbon, $CCl^4 + H^2S = 2HCl + CSCl^2$ (Kolbe).—4. Dissolved in weak alcohol and treated with *amalgam of potassium*, it gives off part of its chlorine to the potassium, and yields chloroform, $CHCl^3$, mono-chlorinated chloride of methyl, CH^2Cl^2, and marsh-gas (Regnault).—5. Treated in a flask provided with an upright condensing tube with *zinc and dilute acid*, it yields hydrochloric acid and chloroform, the latter being converted by the further reducing action of the mixture, into a body containing still less chlorine, probably CH^2Cl^2 (Geuther, *loc. cit.*)—6. It is not decomposed by aqueous potash or sulphydrate of potassium; but *alcoholic potash* slowly converts it into chloride and carbonate of potassium (Regnault). Heated with alcoholic potash to 100° C. in a sealed tube for a week, it is partly converted into ethylene (Berthelot, Ann. Ch. Pharm. cix. 118).—7. Heated to 170° or 180° C. with 3 vols. *phenylamine*, it yields carbotriphenyltriamine (Hofmann, Proc. Roy. Soc. ix. 284):

$$\underset{\text{Phenylamine.}}{6(N.H^2.C^6H^5)} + CCl^4 = \underset{\substack{\text{Hydrochlorate of carbotri-}\\ \text{phenyltriamine.}}}{[N^3.\overset{''''}{C}.(C^6H^5)^3.H^2].HCl} + \underset{\substack{\text{Hydrochlorate of}\\ \text{Phenylamine.}}}{3[(N.H^2.C^6H^5).HCl].}$$

8. With *triethylphosphine* it yields a white crystalline product. (Hofmann, *ibid.* x. 184.)

A compound, CCl^4SO^2, formed by the action of moist chlorine on sulphide of carbon, sometimes regarded as *sulphite of tetrachloride of carbon*, but more probably a chlorinated derivative of *methyl-sulphurous acid*, will be described under that head.

TRICHLORIDE OF CARBON. C^2Cl^6. *Sesquichloride of Carbon, Perchloride of Carbon, Perchlorinated Chloride of Ethylene, Chlorure de Chloroxéthose.*—This compound, which was discovered and investigated by **Faraday** (Phil. Trans. 1826, p. 47), and further by **Regnault** (Ann. Ch. Phys. [2] lxix. 166; lxxxi. 371), is produced by the action of chlorine in sunshine on various compounds and derivatives of ethyl and ethylene: 1. On dichloride of carbon, C^2Cl^4 (**Faraday**).—2. On chloride of ethylene: $C^2H^4Cl^2 + 4Cl^2 = 4HCl + C^2Cl^6$; the action also takes place, though more slowly in diffused daylight (**Faraday**), or with aid of heat (**Liebig**).—3. On chloride of ethyl, first in the shade, afterwards in sunshine: $C^2H^5Cl + 5Cl^2 = 5HCl + C^2Cl^6$ (**Laurent**, Ann. Ch. Phys. [2] lxxxiv. 328); similarly on mono-, di-, or tri-chlorinated chloride of ethyl (**Regnault**).—4. On sulphite of ethyl, with simultaneous formation of chloride of sulphuryl, chloraldehyde, and hydrochloric acid (**Ebelmen and Bouquet**, Ann. Ch. Phys. [3] xvii. 66):

$$(C^2H^5)^2SO^3 + 11Cl^2 = C^2Cl^6 + SO^2Cl^2 + C^2Cl^4O + 10HCl.$$

5. On oxide of ethyl, which, in bright sunshine, is sometimes converted at once into sesquichloride of carbon and chloraldehyde, sometimes into perchlorethylic oxide, $C^4Cl^{10}O$, 1 at. of which is resolved by distillation into C^2Cl^4O and C^2Cl^6 (**Regnault**, **Malaguti**). Several perchlorinated compound ethers (carbonic, succinic, &c.) also yield trichloride of carbon, when similarly treated.—6. On hydrochlorate of ethylamine:

$$C^2H^7N + 5Cl^2 = C^2Cl^6 + NH^4Cl + 3HCl.$$

The sal-ammoniac is ultimately resolved by the excess of chlorine into hydrochloric acid and nitrogen, which escapes, a certain portion, being, however, converted into chloride of nitrogen (**Geuther** and **Hofacker**, Ann. Ch. Pharm. cviii. 51). The formation of chloride of nitrogen must render the process dangerous.—7. Tetrachloride of carbon passed through a red-hot tube is resolved into the trichloride and free chlorine (p. 765).

Preparation.—1. Chloride of ethylene is exposed to the sun in a bottle filled with chlorine, water being frequently added in small portions to absorb the hydrochloric acid produced, and the chlorine frequently renewed as long as any action is perceptible. The crystalline product is washed with water, pressed between bibulous paper, heated to sublimation, then dissolved in alcohol, precipitated by water containing potash, again washed with water, pressed, and dried in vacuo over sulphuric acid (**Faraday**). By passing chlorine through chloride of ethylene, heated nearly to the boiling point, part of that compound is converted into trichloride of carbon, which crystallises out for the most part on cooling the liquid with ice (**Liebig**, Ann. Ch. Pharm. i. 219).—2. A bottle filled with chlorine, and containing a little chloride of ethyl, is set aside in the shade for twenty-four hours, the chlorine then renewed and the vessel exposed to the sun: such exposure at the beginning of the process would produce explosion (**Laurent**). Or better: vapour of chloride of ethyl produced by heating alcohol with strong hydrochloric acid, and purified by passing through water and oil of vitriol, is brought in contact with chlorine in a vessel exposed to the summer sun (**Regnault**).—3. Perchlorethylic oxide ($C^4Cl^{10}O$) is distilled, and the distillate is repeatedly treated with water, which takes up chloraldehyde and leaves trichloride of carbon. (**Malaguti**, Ann. Ch. Phys. [3] xvi. 6, 14.)

Properties.—Trichloride of carbon crystallises in right rhombic prisms ∞P, modified by the faces $\infty \breve{P} \infty$ and the horizontal prism $P \infty$. Angles of the prism $\infty P =$ 58° and 122° (**Brooke**); 59° and 121° (**Laurent**). The crystals are colourless, transparent, and nearly tasteless, but have an aromatic camphorous odour. They are as hard as sugar, and easily pulverised. Specific gravity = 2·0. Refracting power = 1·5767. They do not conduct electricity. They melt at 160° C.; boil and sublime at 182°, and volatilise even at ordinary temperatures. Vapour-density = 8·157, corresponding to 2 volumes $\left(\frac{2\,.\,12 + 6\,.\,35{\cdot}5}{2} \times 0{\cdot}0693 = 8{\cdot}212\right)$. Insoluble in water, soluble in alcohol, still more in ether; the solutions are not clouded by nitrate of silver. Soluble also in oils, both fixed and volatile.

Decompositions.—1. By repeated distillation, or by passing its vapour through a red-hot porcelain tube, the trichloride is resolved into the dichloride, C^2Cl^4, and free chlorine.—2. It burns with a red light in the flame of a spirit-lamp, but is extinguished on removal.—3. Passed, together with *hydrogen*, through a red-hot tube, it yields hydrochloric acid and dichloride of carbon (**Geuther**), and undergoes a similar decomposition when heated with *sulphur*, *phosphorus*, or *iodine*.—4. Most *metals* heated in the vapour of the trichloride are converted into chlorides, with separation of charcoal.—5. The vapour passed over red-hot *baryta*, *strontia*, or *lime*, yields a chloride and carbonate of the metal, with deposition of charcoal; with *oxide of zinc*, it sometimes forms oxychloride of carbon; with the *oxides of copper* and *mercury*, and with *peroxide of lead*, the products are metallic chloride and carbonic anhydride.—6. The trichloride is not altered by distillation with aqueous or alcoholic potash; but when gently heated with an alcoholic solution of *sulphydrate of potassium*, it yields dichloride of carbon, together with chloride of potassium, sulphydric acid, free sulphur, and a brown sulphur compound, apparently resulting from a secondary action (**Regnault**):

$$C^2Cl^6 + 2KHS = C^2Cl^4 + 2KCl + H^2S + S.$$

7. Heated in sealed tubes with 8 at. *hydrate of potassium*, it yields oxalate and chloride of potassium:

$$C^2Cl^6 + 8KHO = C^2K^2O^4 + 6KCl + 4H^2O;$$

but the decomposition is very imperfect, even when the mixture is heated to between 210° and 220° C. for several days (**Geuther**, Ann. Ch. Pharm. lx. 247).—8. Heated to 100° C. in sealed tubes with *alcoholic potash*, it yields the same products, together with hydrogen gas and ethylene (**Berthelot**, Ann. Ch. Pharm. cix. 118). The principal reaction is probably represented by the equation:

$$C^2Cl^6 + 7KHO + C^2H^5.K.O = C^2K^2O^4 + 6KCl + 4H^2O + C^2H^4,$$

and the free hydrogen results from a secondary decomposition, a number of liquid products and brown insoluble substances being formed at the same time. Trichloride of carbon is not attacked by ammonia, nitric acid, or sulphuric acid. Boiling nitric acid dissolves it, part separating on cooling, the rest on addition of water. In contact with chlorine and water, it does not yield trichloracetic acid.

DICHLORIDE OF CARBON. C^2Cl^4. *Protochloride of Carbon, Perchlorethylene, Chlorēthose.*—Discovered and examined by **Faraday** (Phil. Trans. 1821, p. 47), further by **Regnault** (Ann. Ch. Phys. [2] lxx. 104; lxxxi. 372). It is produced by the action of a red heat on the trichloride or tetrachloride of carbon, either alone or in presence of hydrogen (pp. 765, 766); by the action of nascent hydrogen on the trichloride at ordinary temperatures; also by that of alcoholic sulphydrate of potassium on the trichloride, and of alcoholic potash on the tetrachloride (p. 765).

Preparation.—1. Vapour of trichloride of carbon is passed through a red-hot tube filled with fragments of glass, whereupon a large quantity of chlorine is set free, and the dichloride passes over in the form of a liquid coloured yellow by chlorine. It is purified by passing it several times through the red-hot tube, then shaking it up with mercury, and rectifying at as low a temperature as possible (**Faraday**).—2. The trichloride is added by small portions to an alcoholic solution of sulphydrate of potassium, and, as soon as the evolution of sulphuretted hydrogen has ceased, the liquid is distilled, and the alcoholic distillate diluted with water: the dichloride then separates in the form of a heavy liquid: this process is easier than the preceding (**Regnault**).—3. Trichloride of carbon is mixed with water and granulated zinc, and sulphuric acid added from time to time with agitation, till all the trichloride is decomposed. On subsequently distilling the liquid, dichloride of carbon passes over with the aqueous vapour. (**Geuther**, Ann. Ch. Pharm. cvii. 212.)

Properties.—Very mobile liquid, of specific gravity 1·619 at 20° C. (**Regnault**), 1·612 at 10° (**Geuther**). Refracting power = 1·4875 (**Wollaston**). It does not conduct electricity. It remains liquid at −18° C.; boils at 122° (**Regnault**), 116·7° (**Geuther**). Vapour-density, by experiment = 5·82, corresponding to 2 volumes. $\left(\frac{2\,.\,12 + 4\,.\,35{\cdot}5}{2} \times 0{\cdot}0693 = 5{\cdot}75.\right)$ It is insoluble in water, acids, and aqueous alkalis, but dissolves in alcohol, ether, and oils, both fixed and volatile.

Decompositions.—1. At a red heat it is resolved into free chlorine and the protochloride, C^2Cl^2.—2. When its vapour is passed over red-hot *baryta*, vivid ignition takes place, with formation of chloride of barium and carbonic anhydride, and separation of charcoal.—3. Heated for some time to 200° C., with 6 at. *hydrate of potassium*, it is completely converted into oxalate and chloride of potassium, with evolution of hydrogen gas (**Geuther**, Ann. Ch. Pharm. cx. 247):

$$C^2Cl^4 + 6KHO = C^2K^2O^4 + 4KCl + 2H^2O + H^2.$$

4. It absorbs dry chlorine in sunshine, forming the trichloride, C^2Cl^6; but if exposed to an atmosphere of chlorine under a layer of water, it yields trichloracetic acid. (**Kolbe**, Ann. Ch. Pharm. liv. 181):

$$C^2Cl^4 + 2H^2O + Cl^2 = C^2HCl^3O^2 + 3HCl.$$

5. It absorbs bromine in sunshine, yielding chlorobromide of carbon, $C^2Cl^4Br^2$.

PROTOCHLORIDE OF CARBON, C^2Cl^2. *Subchloride of Carbon, Julin's Chloride of Carbon.*—This compound was discovered in 1821, by Julin, a manufacturer of nitric acid at Abo in Finland, who obtained it accidentally in distilling crude nitre with burnt green vitriol in cast-iron retorts, the cast-iron probably furnishing the carbon, and the crude nitre the chlorine (Ann. Ch. Phys. [2] xviii. 269). It was more exactly investigated by Phillips and Faraday (Phil. Trans. 1821), and afterwards by Regnault (Ann. Ch. Phys. [2] lxx. 104), who prepared it by passing vapour of chloroform or of dichloride of carbon, through a strongly ignited porcelain tube filled with fragments of porcelain, dissolving the crystalline product in ether, filtering, evaporating to dryness, and subliming. In performing this process, care must be taken not to heat the porcelain tube too strongly; otherwise, no chloride of carbon will be obtained, but only a deposit of charcoal.

Properties.—Protochloride of carbon forms white, delicate needles, apparently four-sided, having a silky lustre. It melts, boils, and sublimes between 175° and 200° C., but may be sublimed without fusion at 120°, the sublimate then consisting of long needles. It has a peculiar odour, something like that of spermaceti, but no taste. In the cold it is almost inodorous. It is insoluble in water, but very soluble in alcohol; dissolves also in ether, and in hot oil of turpentine, whence it crystallises in needles on cooling.

The alcoholic solution does not precipitate nitrate of silver.

The vapour passed through a red-hot porcelain tube filled with fragments of rock-crystal, is resolved into chlorine and charcoal. The compound burns with bluish colour in the flame of a candle, but ceases to burn when withdrawn. It is not decomposed or dissolved by nitric, hydrochloric, or sulphuric acid, or by boiling potash. Chlorine does not act upon it, even in sunshine. Potassium burns in its vapour with intense ignition, forming chloride of potassium and depositing charcoal.

Berthelot regards this compound, not as C^2Cl^2, but as $C^{10}Cl^{10}$. The vapour-density does not appear to have been determined.

CARBON, CHLOROBROMIDE OF. $C^2Cl^4Br^2$. *Bromide of Perchorethylene, Bromure de Chloroxéthose.* (Malaguti, Ann. Ch. Phys. [3] xvi. 14.)—Dichloride of carbon exposed to sunshine in contact with bromine solidifies in a few hours to a crystalline mass, which may be purified by repeated crystallisation from alcohol. The crystals resemble those of C^2Cl^6; they have a specific gravity of 2·3 at 21° C., taste slightly aromatic, begin to volatilise at 100°, decompose at about 200° into bromine and the dichloride, and when treated with protosulphide of potassium are resolved into bromide of potassium and dichloride of carbon:

$$C^2Cl^4Br^2 + K^2S = C^2Cl^4 + 2KBr + S.$$

CARBON, DETECTION AND ESTIMATION OF. The methods of detecting and estimating carbon and its compounds have been already described under the head of ANALYSIS.

If the carbon is not already in the form of carbonic anhydride or a carbonate, it is converted into carbonic anhydride by combustion, either in an atmosphere of oxygen or with oxide of copper or chromate of lead, the amount of carbonic anhydride thereby produced being estimated by absorption in strong potash-ley (ANALYSIS, ORGANIC, pp. 225—238). This method serves for the estimation of carbon in cast-iron and other metallic compounds, as well as in organic bodies. *Gaseous carbon-compounds*, such as carbonic oxide and hydrocarbons, are converted into carbonic anhydride by explosion with excess of oxygen, the amount of that compound produced being then determined by absorption with potash. (ANALYSIS, VOLUMETRIC, OF GASES, pp. 286—288.)

Carbonates are decomposed with dilute sulphuric or hydrochloric acid, and the carbonic anhydride thereby evolved is usually determined by loss (see ACIDIMETRY, p. 38, and ALKALIMETRY, p. 149). The presence of carbonates in any mixture, solid or liquid, is detected by the effervescence which ensues on addition of dilute sulphuric or hydrochloric acid. This effervescence may, however, arise from the escape of sulphydric acid or sulphurous anhydride, if sulphides or sulphites are also present. These gases are readily distinguished from carbonic anhydride by their peculiar odours; sulphydric acid also by its property of blackening lead-salts. To detect carbonic anhydride when evolved together with one or both of these gases, the gaseous mixture is passed into baryta-water. If a precipitate is formed, carbonic or sulphurous acid may be present or both; if the former alone, the precipitate will be completely soluble in hydrochloric acid, *after treatment with chlorine-water;* but if sulphurous acid is also present, it will be oxidised by the chlorine-water, and converted into sulphuric acid, which will then form sulphate of barium, insoluble in hydrochloric acid.

The amount of carbonic anhydride in a gaseous mixture is ascertained directly by absorption with potash, sulphurous anhydride or sulphydric acid, if present, having been previously removed by absorption with peroxide of manganese (p. 282).

Carbonic acid in solution, either free or combined, in a mineral water for example, is estimated by adding ammonia and chloride of calcium, and leaving the liquid to itself in a corked flask for several hours. The carbonic acid is thereby precipitated as carbonate of calcium, containing 43·88 per cent. CO^2.

To estimate the carbonic acid in the air, a large quantity of air, the volume being measured by an aspirator (p. 427), is passed through a series of weighed potash-bulbs. Another method is to shake up a quantity of air in a closed vessel of known capacity, with an excess of lime-water of known strength, and then determine the quantity of lime remaining uncombined by means of a standard solution of oxalic acid. This method is easy of execution, and affords the means of quickly determining the varying amount of carbonic acid in the several parts of an inhabited apartment at different times.

Atomic Weight of Carbon.—Three methods have been adopted for determining the atomic weight of carbon: 1. From the quantity of carbonic anhydride produced by the combustion of a given weight of carbon.—2. By comparing the weights of equal volumes of carbonic anhydride and oxygen, it being supposed that carbonic anhydride contains its own volume of oxygen.—3. From the weight of metallic silver obtained by the combustion of organic silver-salts.

Of these methods the first is considered the most trustworthy. The amount of carbonic anhydride produced by the combustion of carbon was determined with a very near approximation to the truth by Lavoisier in 1775, afterwards with more or less accuracy by Guyton-Morveau (1785), Clément and Desormes (1802), Allen and Pepys (1807), and Saussure (1809); but the most exact determinations are those made by Dumas and Stas (Ann. Ch. Phys. [3] i. 1), and by Erdmann and Marchand (J. pr. Chem. xxiii. 159). These chemists burned weighed quantities of diamond or graphite with oxide of copper and oxygen gas, and weighed the carbonic anhydride taken up by the potash-apparatus, after it had been freed from a very small quantity of admixed water by passing over chloride of calcium or sulphuric acid. The small quantity of residual ash was deducted from the weight of the carbon employed, and the quantity of water produced in the combustion likewise taken into account.

In this manner the quantity of carbon which combines with 200 pts. of oxygen to form carbonic anhydride was found by Dumas and Stas, in fourteen experiments, to vary only between the limits 74·87 and 75·12, the mean result being 75·005, with a probable error of ± 0·013. Erdmann and Marchand, in nine experiments similarly conducted, obtained numbers varying between 74·84 and 75·19, the mean being 75·028. Now since, of the two oxides of carbon, carbonic anhydride contains, with the same quantity of carbon, twice as much oxygen as carbonic oxide, these compounds may be represented by the formulæ CO^2 and CO, a view of their constitution, which is likewise in accordance with that of the other compounds of carbon. Hence, from the above-mentioned results respecting the composition of carbonic anhydride, it follows that if the atomic weight of oxygen = 100, that of carbon will be 75, and on the hydrogen scale:

$$\begin{array}{lll} \text{If} & O = 8, & C = 6 \\ \text{and if} & O = 16, & C = 12. \end{array}$$

The reason for adopting the numbers in the last line are fully detailed in the article **Atomic Weights** (pp. 459—462).

The second method of determining the atomic weight of carbon was first adopted by Berzelius and Dulong in 1819. From specific gravity determinations then made it was concluded that equal volumes of carbonic anhydride and oxygen weighed 1·5425 and 1·1026 respectively; and assuming that carbonic anhydride contained its own volume of oxygen, the difference of the two numbers gave the weight of the carbon in the same volume, whence it was calculated that the atomic weight of carbon on the oxygen scale (O = 100) was 76·528, which number was adopted as correct for twenty years. In 1841, Wrede, following the same method, but taking into account the more exact coefficients of expansion of the gases determined by Rudberg, Magnus, and Regnault, obtained the number 75·12. Determinations not much differing from this were made in like manner by other experimenters; but the method is not capable of yielding very exact results, because the alterations of volume sustained by oxygen and carbonic anhydride for equal variations of temperature and pressure are not equal, and consequently the assumption that oxygen, in being converted into carbonic anhydride, undergoes no change of volume, cannot be true for all temperatures.

The third method, founded on the analysis of the silver-salts of organic acids, was adopted by Liebig and Redtenbacher (Ann. Ch. Pharm. xxxviii. 116). Assuming Ag = 1351 and H = 12·48 (O = 100), these chemists obtained as the mean result of their analyses, C = 75·854. The more exact determinations since made of the atomic weight of silver would lead to a slight alteration in this result. Strecker, from the same experiments, and without assuming the atomic weights of silver as previously known, calculated the atomic weight of carbon as = 75·415; but this method, as well as the second, is not considered so trustworthy as the first, the result of which, obtained by Dumas and Stas is now universally adopted.

CARBON, IODIDE OF. No compound of carbon and iodine has yet been obtained. Iodoform, CHI^3, was formerly supposed to be an iodide of carbon, the hydrogen contained in it having been overlooked. (Gm. vii. 335.)

CARBON, NITRIDE OF. Only one compound of carbon and nitrogen is known with certainty, viz. CYANOGEN, CN (*q. v.*) Many cyanogen-compounds yield by calcination a residue called mellone, which Liebig regards as a nitride of carbon containing C^3N^4. It does not, however, appear to have been obtained quite free from hydrogen (see MELLONE and MELLONIDES). According to Thaulow, a peculiar nitride of carbon, isomeric, but not identical with cyanogen, is obtained by ignition of cyanide of silver (see CARBAZOTE, p. 757).

CARBON, OXIDES OF. Two oxides of carbon are known, the protoxide CO, and the dioxide, or carbonic anhydride, CO^2, commonly called *carbonic acid.* Both are produced by the direct combination of carbon and oxygen; the former is known only in the gaseous state: the latter is gaseous at ordinary temperatures.

DIOXIDE OF CARBON. CARBONIC ANHYDRIDE, CO^2. *Anhydrous Carbonic acid, Fixed air, Mephitic air, kohlensaures gas, Kohlensäure, Gas sylvestre, Spiritus sylvestris.*—The evolution of this gas in the burning of lime and in fermentation, was known to Paracelsus and Van Helmont, the latter of whom gave it the name of *gas sylvestre;* its properties were afterwards investigated by Hales, Black, Cavendish, Priestley, and Bergmann, but its true composition was first demonstrated by Lavoisier, who showed that it was a compound of carbon and oxygen, containing 28 per cent. carbon and 72 oxygen, numbers approaching very nearly to the proportions now received as correct, viz. 27·27 carbon to 72·73 oxygen (p. 769).

Carbonic anhydride is formed by the combustion of carbon in oxygen gas, or in the air. It is a constant product of the ordinary processes of combustion, inasmuch as all substances used for fuel, such as wood, coal, oil, wax, tallow, &c. contain carbon. It is likewise formed by the respiration of animals, in various processes of fermentation, as in the preparation of wine and beer, and by the decay of animal and vegetable substances. It issues from fissures in the ground, in various localities, chiefly in volcanic districts, and is ejected in enormous quantities from the craters of active volcanos. From all these sources it is continually being poured into the atmosphere, of which it therefore forms a constant constituent: the average amount of it contained in the air in the open country, is 4 volumes in 10,000; in the air of crowded towns, it is often much greater (p. 437). It exists also in larger proportion at the bottom of wells, mines, quarries, and caverns, especially in limestone districts, where it is evolved from fissures and does not readily escape, in consequence of its greater density. Carbonic anhydride (or acid), exists also in solution in all natural waters, some, as those of Seltz, Vichy, and Spa, containing it in such quantity as to give them an effervescing character. Lastly, it is produced by the decomposition of carbonates, either by heat or by the action of the stronger acids, and is a frequent product of the decomposition of organic bodies at high temperatures.

Preparation.—The easiest way of obtaining the gas is to decompose chalk, or marble, with hydrochloric acid, in an ordinary generating vessel, provided with a gas-delivery tube:

$$Ca^2CO^3 + 2HCl = 2CaCl + CO^2 + H^2O.$$

Dilute sulphuric acid may also be used, but it is less convenient, as the sulphate of calcium produced forms a hard mass in the vessel, which is difficult to extract, whereas chloride of calcium is easily soluble: moreover, the chloride is more useful as a residual product. The gas may be received over water, or, as it is very heavy, it may be collected by simple displacement of the air, the delivery-tube being bent vertically downwards, so as to reach to the bottom of the receiver. This is also the most convenient mode of collection when the gas is required dry, a desiccating tube containing dry chloride of calcium or pumice-stone soaked in oil of vitriol, being interposed between the generator and receiver. On the large scale, carbonic anhydride may be obtained by heating chalk or marble to redness, in an iron or earthen retort.

Properties.—Carbonic anhydride is, at ordinary temperatures and pressures, a colourless gas, but may be liquefied by cold or pressure (p. 771). Its specific gravity in the gaseous state is 1·5241 (Regnault), being rather more than $1\frac{1}{2}$ times that of air. In consequence of this great density, it may be poured from one vessel to another like a liquid, and often collects at the bottom of wells, mines, and caverns, as in the *Grotto del Cane* near Naples, the atmosphere of which, within about a foot of the ground, is highly charged with the gas, while the upper part is comparatively free.

From the experiments of Regnault, it appears that the density of carbonic anhydride does not vary in the same proportion as the pressure, excepting within narrow limits: under a pressure of several atmospheres, the deviation from this law is very perceptible. The coefficient of expansion by heat between 0° and 100° C. is 0·3719 (Regnault); 0·366087 (Magnus); refracting power = 1·526 (Dulong).

Carbonic anhydride does not affect the colour of *litmus-paper*, when both are quite dry; but if moisture is present, the blue colour of the paper changes to wine-red, like that produced by boric acid: on exposure to the air, however, the redness disappears, in consequence of the escape of the gas. *Lime-water* introduced into the gas is immediately rendered turbid, in consequence of the formation of neutral carbonate of calcium, but if an excess of the gas is present, the liquid becomes clear again after a while, especially if shaken, an acid carbonate being then formed, which is soluble in water. Solution of *potash*, or a lump of moist solid potash, introduced into the gas standing over mercury, rapidly absorbs it. It dissolves in about its own volume of *water* at ordinary temperatures, and in less than $\frac{1}{2}$ of its volume of *alcohol*.

Carbonic anhydride is irrespirable; animals immersed in it soon die, not only from want of oxygen, but in consequence of a direct poisonous action, violent spasms being sometimes produced, sometimes complete atony of the cerebral faculties. Mixed with *air*, as it escapes from effervescing liquids, it produces a pungent sensation in the respiratory organs, but it cannot be said to have any decided odour. It is incombustible, and immediately extinguishes a burning taper, also the flame of sulphur or phosphorus: but *potassium* heated to redness in the dry gas, decomposes it completely, burning with a red light, and producing a deposit of charcoal mixed with carbonate of potassium. *Sodium* decomposes it in like manner, but without becoming red-hot. *Phosphorus* and *boron*, in presence of an alkali, likewise abstract all the oxygen at a red heat. *Hydrogen*, *charcoal*, *iron*, and *zinc*, at a red heat, abstract half the oxygen, converting the carbonic anhydride into carbonic oxide. It is also resolved into carbonic oxide and oxygen by the passage of electric sparks, if hydrogen gas, mercury, or some other metal is present to take up the oxygen; otherwise, the spark immediately causes the gases to recombine. *Growing plants*, or the leaves and other green parts separated from the plant, but still in the fresh state, decompose carbonic anhydride completely under the influence of daylight, and more rapidly in direct sunshine, abstracting the whole of the carbon, and setting the oxygen free. If some fresh leaves of any plant be placed in an inverted receiver, filled with water containing carbonic acid, and standing over water, and the whole be exposed to the sun, a considerable quantity of oxygen gas will collect at the top of the receiver in a few hours. This action of growing plants is the chief cause which prevents the continual accumulation of carbonic anhydride in the atmosphere, and keeps the proportion of it nearly constant. (See ATMOSPHERE, p. 438.)

Respecting the mode of determining the composition of carbonic anhydride, see p. 769. Its density corresponds to 2 volumes of vapour:

$$\frac{12 + 2 \,.\, 16}{2} \times 0{\cdot}0693 = 22 \times 0{\cdot}0693 = 1{\cdot}5246$$

and at pressures and temperatures considerably above its liquefying point, it contains a volume of oxygen exactly equal to its own.

Liquid Carbonic Anhydride.—Carbonic anhydride passes to the liquid state at 0° C. under a pressure of 36 atmospheres. Faraday effected the liquefaction by evolving the gas from carbonate of ammonia, by the action of sulphuric acid in a sealed tube (see GASES, CONDENSATION OF), but the method is dangerous, and yields but a small quantity. The liquid acid is however obtained safely and in large quantity, by the method of Thilorier (Ann. Ch. Pharm. xxx. 122). The apparatus consists of two very strong cylinders, capable of holding 6 litres or pints, made of cast-iron, or better, of lead sheathed with copper, and strengthened with a wrought-iron armature; they rest by two pins placed at the middle of their length on cast-iron supports, so that they may be placed either vertically or horizontally, and swung backwards and forwards. Into one of these cylinders is introduced 1800 grammes of acid carbonate of sodium, and 4 litres of water (or $4\frac{3}{4}$ lbs. of the soda-salt, and 7 pints of water), and a copper tube containing 1000 grammes (or $2\frac{1}{4}$ lbs.) of strong sulphuric acid, is likewise introduced in a vertical position. The cylinder is then tightly closed by a cock of peculiar construction, and swung to and fro, to cause the acid to mix gradually with the carbonate. The gas is then evolved, and not being able to escape, becomes so much condensed that it passes to the liquid state. This part of the operation requires care, as, if the mixture be made too rapidly, great heat will be evolved, and the tension of the gas enormously increased. A fatal accident happened in Paris from this cause. When the action is supposed to be complete, the generating cylinder is made to communicate, by means of a copper tube, with the second cylinder, which is placed horizontally, and provided with a stopcock like the first. This cylinder being slightly cooled, the carbonic anhydride distils over from the first, which is still warm, and condenses in the liquid state. After about a minute the cocks are closed, the cylinders separated, the charge in the first renewed; and this series of operations is repeated several times, till the second cylinder is about two-thirds filled with liquid carbonic anhydride.

Liquid carbonic anhydride is colourless and very soluble in alcohol, ether, and volatile oils, but does not mix with water. Specific gravity 0·90 at −20° C.; 0·83 at 0° C.; 0·60 at + 30° C. (Thilorier). Its tension at different temperatures is shown in the following table.

Temp. C.	Tension in Atmospheres.		Temp. C.	Tension in Atmospheres.	
	Faraday.	Mareska and Donny.		Faraday.	Mareska and Donny.
−59·4°	4·6		−5·0°	33·1	36
48·8	7·7		0·0	38·5	42
36·6	12·5		+6·3		46
30.5	15·4		10·0		52
26·1	17·8		15·5		57
20·0	21·5	23·6	19·0		63
15·0	24·7	25·3	23·5		68
12·2	26·8		27·0		74
10·0		27·5	30·7		80
9·4	29·1		34·5		

Solid Carbonic Anhydride.—When the liquid anhydride is suddenly relieved from the pressure under which alone it can exist, part of it flashes instantly into vapour, and in so doing produces so great a degree of cold, that the remaining portion of the liquid solidifies. To obtain the solid anhydride, the receiver containing the liquid is provided with a tube passing through its side, and reaching nearly to the opposite side, so that when the cylinder is set horizontally, this tube dips into the liquid. On opening a stopcock provided for the purpose, a quantity of the liquid is forced out by the pressure of the gas above it, and forms a white cloud of the solid anhydride, as it issues into the air. By causing this jet of vapour to pass into a cylindrical metal box, having within it an inclined metal tongue, against which the jet of liquid and vapour impinges, and is thus made to circulate within the box for some little time before it finally escapes, a considerable quantity of the solid anhydride may be collected in the form of a white flocculent mass like snow.

Solid carbonic anhydride may be left exposed to the air for some little time without evaporating, because, like all flocculent substances, it conducts heat but slowly. Its tension is 1·14 atmospheres at − 99·4° C.; 1·36 at −77·2°; 2·28 at −70·5°; 3·6 at −63·2°; 4·6 at −59·4°; 5·33 at −57·0 (Faraday). An air or spirit thermometer immersed in it sinks to −78° C. Notwithstanding this low temperature, the solid substance may be placed on the hand without occasioning a very acute sensation of cold, because it does not come into close contact with the skin, being separated from it by a film of vapour; but if pressed between the fingers, it produces a very painful sensation, and raises a blister like a burn. By mixing it with ether, its heat-conducting power is greatly increased; it therefore evaporates more quickly, and produces much more powerful frigorific effects. Mercury poured into it solidifies instantly to a mass like lead. The cold which it produces is sufficient to liquefy sulphydric acid, chlorine, nitrous oxide, and several other gases. The intensity of the cold may be still further increased by placing the mixture under an exhausted receiver. The temperature then sinks to a degree at which the liquid anhydride is not more volatile than water at 30° C., and alcohol assumes the consistence of a thick oil, but does not solidify. By exposing to this bath, tubes of glass or copper in which gases have been compressed by a forcing pump to 40 atmospheres, Faraday has succeeded in liquefying all the known gases, excepting oxygen, hydrogen, nitric oxide, carbonic oxide, and marsh-gas, and in solidifying a considerable number of them. Carbonic anhydride itself exposed to this temperature and pressure, is reduced to a vitreous transparent mass.

Carbonic Acid.—Gaseous carbonic anhydride dissolves in about its own volume of water at ordinary temperatures, forming a solution of specific gravity 1·0018. It has a sharp and slightly acid taste, turns the blue colour of litmus to wine-red, partially neutralises alkalis, and dissolves the carbonates of barium, strontium, calcium, magnesium, &c. It, therefore, possesses *acid* properties, and from the composition of the carbonates, we may infer that it contains an acid of the composition H^2CO^3. But this acid cannot be isolated, as heat, diminished pressure, or congelation immediately resolves it into water and carbonic anhydride. In short, carbonic acid as a definite compound cannot be said to be known.

The volume of carbonic anhydride dissolved by water at a given temperature, is nearly the same under all pressures; consequently the weight of the gas absorbed increases in nearly the same proportion as the pressure. This rule must not, however, be understood as strictly true, for Regnault has shown that the volume of carbonic anhydride does not vary exactly in the inverse ratio of the pressure.

Under a given pressure, the volume of gas absorbed diminishes as the temperature rises. At the boiling heat, the whole of the gas is driven off; hence carbonic acid water holding an earthy carbonate in solution deposits it when the liquid is boiled. This is the cause of the furring of kettles, boilers, &c., in which spring or river-water containing carbonate of calcium dissolved in this manner, is boiled.

The coefficients of absorption of carbonic anhydride, that is to say the volumes (reduced to 0° C. and 0·760 met.) which 1 vol. of water absorbs under the pressure of 0·760 met. and at various temperatures, are as follows:

Temp.	Vol. of Gas absorbed.	Temp.	Vol. of Gas absorbed.
0° C.	1·7697	12° C.	1·1018
2	1·6481	14	1·0321
4	1·5126	16	0·9753
6	1·3901	18	0·9318
8	1·2809	20	0·9013
10	1·1847		

(Bunsen's Gasometry. See also the article GASES, ABSORPTION OF.)

Water which has been saturated with carbonic acid under pressure, gives it up with brisk effervescence as soon as the pressure is removed. The various kinds of aërated water, *soda-water*, *effervescing lemonade*, &c., consist of water impregnated by mechanical pressure with large quantities of carbonic acid, and flavoured with various saline and other ingredients. (For a description and figure of Tylor's soda-water machine, see *Ure's Dictionary of Arts, Manufactures and Mines*, iv. 728.) Champagne and other effervescing wines and bottled beer likewise owe their sparkling properties to the presence of this gas; but in these liquids the carbonic acid is produced by the fermentation itself, the wine or beer being bottled before the fermentation is complete, whereby a considerable quantity of the gas, which would otherwise escape into the air, is retained.

For the behaviour of aqueous carbonic acid to bases, see CARBONATES.

PROTOXIDE OF CARBON. CARBONIC OXIDE. CO.—This compound, which is known only in the gaseous state, was discovered towards the end of the last century by Lassonne and by Priestley; but its true nature was first recognised some years afterwards by Woodhouse (Gilbert's Annalen, ix. 423). It is produced: 1. By the oxidation of carbon at very high temperatures, when the supply of oxygen is not sufficient for the complete conversion of the carbon into carbonic anhydride (p. 763).—2. When carbonic anhydride is exposed to a red heat in contact with hydrogen, carbon, metals, or other bodies which can abstract part of the oxygen: hence it is always produced in charcoal or coke fires, when the draught of air has to pass upwards through a considerable mass of red-hot fuel, and is the cause of the blue flame almost always seen on the top of such fires.—3. It is also formed, together with hydrogen and carbonic anhydride, when vapour of water is passed over red-hot coke or charcoal. A sample of the gaseous mixture thus formed was found by Bunsen to contain 56·03 volumes per cent. of hydrogen, 29·15 carbonic oxide, 14·65 carbonic anhydride, and 0·17 carburetted hydrogen.—4. Carbonic oxide is produced, either alone or together with carbonic anhydride, in the reduction of metallic oxides by carbon at a strong red heat. The gas evolved from iron blast-furnaces contains from 25 to 32 per cent., that from copper-refining furnaces from 13 to 19 per cent. carbonic oxide (Bunsen, Pogg. Ann. xlvi. 193; l. 81).—5. In the dry distillation of many organic compounds.—6. In the decomposition of oxalic acid and formic acid by strong sulphuric acid:

$$\underset{\text{Oxalic acid.}}{C^2H^2O^4} = CO + CO^2 + H^2O$$

$$\underset{\text{Formic acid.}}{CH^2O^2} = CO + H^2O$$

7. In the decomposition of crystallised ferrocyanide of potassium by sulphuric acid (Fownes):

$$\underset{\text{Crystallised ferrocyanide of potassium.}}{2K^2FeC^3N^3.3H^2O} + 6H^2SO^4 + 3H^2O = 6CO + \underset{\text{Sulphate of ammonium.}}{3(NH^4)^2SO^4} + \underset{\text{Sulphate of potassium.}}{2K^2SO^4} + \underset{\text{Ferrous sulphate.}}{Fe^2SO^4}$$

Preparation.—1. By heating to redness in a gun-barrel fitted with a gas-delivery tube, a mixture of oxide of iron, zinc, lead, or copper with charcoal or graphite; or of an alkaline or earthy carbonate (chalk for example) with graphite, charcoal, or iron filings; or by passing carbonic anhydride repeatedly over red-hot iron or charcoal. By either of these methods, carbonic oxide is obtained mixed with carbonic anhydride, from which it may be freed by passing the gas through milk of lime or strong potash; it may then be collected over water. The charcoal used must be previously well ignited to free it from moisture and absorbed gases.—2. By heating in a flask a mixture of oxalic acid, or an oxalate, or a formate, with excess of strong sulphuric acid, and removing the carbonic anhydride evolved when oxalic acid or an oxalate is used, as before.—3. When crystallised ferrocyanide of potassium, in the state of powder, is heated in a flask with eight or ten times its volume of sulphuric acid, carbonic oxide is evolved quite free from carbonic anhydride, and mixed only with a small quantity of vapour of hydrocyanic acid, resulting from another reaction which takes place at the same time, if the quantity of water present is more than sufficient for the above decomposition (see FERROCYANIDES). This is the most convenient mode of preparing carbonic oxide. Care must, however, be taken not to raise the heat higher than is necessary for the complete liquefaction of the mixture; for at that point the evolution of carbonic oxide ceases, and if the heating be continued, the excess of sulphuric acid acts on the ferrous sulphate produced, converting it into ferric sulphate, and being itself reduced to sulphurous anhydride, which escapes as gas and mixes with the carbonic oxide.

Properties.—Carbonic oxide is a colourless gas of specific gravity 0·96799 (Wrede); its molecule CO therefore occupies two volumes:

$$\frac{12 + 16}{2} \times 0{\cdot}0693 = 14 \times 0{\cdot}0693 = 0{\cdot}9702.$$

It is perfectly neutral to vegetable colours, and very sparingly soluble in water, which, according to Bunsen, dissolves only 0·024 or about $\frac{1}{40}$ of its bulk at 15° C. It is a very poisonous gas, acting chiefly on the nervous system, causing giddiness when inhaled, sometimes also acute pain in various parts of the body, and after a while complete asphyxia. According to Leblanc (Ann. Ch. Phys. [3] v. 223), it is to this gas that the suffocating quality of air in which charcoal has been burnt is chiefly due.

Carbonic oxide does not support the combustion of bodies which burn in oxygen, but in contact with the air it takes fire on the approach of a burning body, and burns with a blue flame, producing carbonic anhydride. Mixed with excess of oxygen, it may be exploded by the electric spark, 2 vols. of it then uniting with 1 vol. oxygen and producing 2 vol. carbonic anhydride CO^2. Now as 2 vols. CO^2 contain 2 vols. oxygen, it follows that 1 vol. oxygen must have been derived from the carbonic oxide. Hence carbonic oxide contains half its own volume of oxygen. Now the weight of 2 vols. carbonic oxide, compared with hydrogen, is 28, which, diminished by 16, the weight of 1 vol. oxygen, leaves 12 for the weight of 1 atom of carbon. Hence in carbonic oxide the same weight of carbon is united with exactly half as much oxygen as in carbonic anhydride.

The combustion of carbonic oxide may be brought about by contact with *platinum*. A wire or foil of the metal requires to be heated to 300° C. to induce the combustion: spongy platinum acts at ordinary temperatures, without becoming sensibly heated; but platinum-black introduced into the mixture of carbonic oxide and oxygen becomes red-hot and produces explosion.

Carbonic oxide reduces certain metallic oxides at a red heat, viz. the oxides of copper, lead, tin, iron, &c. It plays indeed an important part in the smelting of many metals, especially of iron.

Carbonic oxide is rapidly absorbed by a solution of *cuprous chloride* in hydrochloric acid, also by ammonical solutions of cuprous salts. This reaction affords an excellent method of removing carbonic oxide from a gaseous mixture (p. 283). It reduces *gold* from the neutral solution of its chloride without the aid of heat.

Carbonic oxide unites directly with *chlorine*, forming oxychloride of carbon or phosgene gas; also with *potassium*. (See POTASSIUM.)

It is absorbed by *hot hydrate of potassium*, yielding formate of potassium, $CO + KHO = CHKO^2$. (Berthelot, Ann. Ch. Pharm. xcvii. 125.)

CARBON, OXYCHLORIDE OF. $COCl^2$ or *Chloride of Carbonyl* $(CO)''.Cl^2$. *Chlorocarbonic oxide. Chlorocarbonic acid. Phosgene.*—This compound was discovered by J. Davy (Phil. Trans. 1812, p. 144), who obtained it by exposing to the sun's rays, a mixture of equal volumes of chlorine and carbonic oxide. The mixture gradually becomes colourless and contracts to half its original volume. The same action takes place slowly in diffused daylight; none whatever in the dark. The name phosgene originally given to the gas signifies a compound formed by light.

Oxychloride of carbon may be more conveniently prepared by passing carbonic oxide into boiling pentachloride of antimony, that compound being at the same time reduced to trichloride. The gas must be received over mercury, as water decomposes it (Hofmann, Ann. Ch. Pharm. lxx. 139). It is likewise produced when carbonic oxide is passed over red-hot chloride of lead or chloride of silver, and in the following decompositions of organic bodies:

a. By the dry distillation of trichloracetates:

$$C^2Cl^3MO^2 = COCl^2 + CO + MCl.$$

b. By the dry distillation of certain perchlorinated methylic ethers, *e. g.* of the *formate*, $C^2Cl^4O^2 = 2COCl^2$; and of the *oxalate*, $C^4Cl^6O^4 = COCl^2 + 3CO$.

c. By the action of a large excess of strong sulphuric acid on the so-called sulphite of tetrachloride of carbon (p. 766):

$$CCl^4SO^2 + H^2O = COCl^2 + 2HCl + SO^2.$$

Oxychloride of carbon is a colourless gas having a suffocating and tear-exciting odour. Its specific gravity is 3·6808 (Davy), 3·4249 (Thomson); calculated for a condensation to two volumes, it is

$$\frac{12 + 16 + 2 \,.\, 35{\cdot}5}{2} \times 0{\cdot}0693 = 3{\cdot}430.$$

Its refracting power is 3·936. It reddens moistened litmus-paper; does not fume in the air.

Oxychloride of carbon is decomposed by *water*, yielding carbonic anhydride and hydrochloric acid:

$$COCl^2 + H^2O = CO^2 + 2HCl.$$

When mixed with an equal volume of hydrogen and half its volume of oxygen, it explodes violently on the passage of an electric spark, yielding the same products. Mixed with oxygen or hydrogen alone, it is not exploded by the electric spark.

Arsenic and *antimony* heated in the gas take up the chlorine, and leave carbonic oxide equal in volume to the original gas. Many metallic oxides, *oxide of zinc*, for example, decompose it with the aid of heat, forming a chloride of the metal and carbonic anhydride equal in volume to the original gas. *Trioxide* of antimony produces trichloride and pentoxide or tetroxide of antimony, leaving carbonic oxide.

By *alcohols* it is converted into chlorocarbonic ethers, *e. g.*:

$$\overset{''}{C}O\left\{\begin{matrix}Cl\\Cl\end{matrix}\right. + \left.\begin{matrix}C^2H^5\\H\end{matrix}\right\}O = \left.\begin{matrix}(CO)''\\C^2H^5\end{matrix}\right\}O + HCl.\\ Cl.$$

With *ammonia gas*, oxychloride of carbon produces carbamide (p. 752) and chloride of ammonium. With *phenylamine* and many other organic bases, it reacts in like manner, forming substitution-derivatives of carbamide.

CARBON, SULPHIDES OF. Only one of these compounds is known with certainty. viz. the disulphide corresponding to carbonic anhydride. The formation of a protosulphide, analogous to carbonic oxide, was announced, in 1857, by Baudrimont, but his statements have not been confirmed. (See page 777.)

DISULPHIDE OF CARBON. CS^2. *Bisulphide of Carbon, Sulphocarbonic Acid.* (Lampadius, Gehlen's N. allg. Journ. d. Chem. ii. 192; Clément and Desormes, Ann. Chim. xlii. 121; Vauquelin and Robiquet, *ibid.* lxi. 145; Berthollet, Thénard, and Vauquelin, *ibid.* lxxii. 252; Berzelius and Marcet, Schw. J. ix. 284; Berzelius, Gilb. Ann. xlviii. 177; Pogg. Ann. vi. 144; Zeise, Schw. J. xxvi. 1; xli. 98, 170; xliii. 160; Couerbe, Ann. Ch. Phys. [2] lxi. 225; Kolbe, Ann. Ch. Pharm. xlv. 53; xlix. 143; Pelouze and Frémy, *Traité de Chimie*, 4ᵐᵉ éd. i. 923).—This compound, which was discovered by Lampadius in 1796, is produced by the direct combination of sulphur and carbon at high temperatures, and in the decomposition of many organic compounds. Sulphur and carbon do not combine when simply heated together in the solid state, because the sulphur volatilises before the requisite temperature is attained; but if charcoal be heated to redness and sulphur-vapour passed over it, the carbon burns in that vapour, forming CS^2.

For preparing small quantities of the disulphide, a porcelain tube is filled with fragments of charcoal, and inserted in an inclined position through a furnace having holes in its sides. The upper extremity of the tube is closed with a cork, and the lower is connected by a bent glass tube, with a bottle containing water, the lower end of the bent tube passing through the cork and dipping just below the surface of the water. When the charcoal is red-hot, the upper end of the tube is opened and a piece of sulphur put in; the sulphur melts and runs down to the lower part of the tube, where it volatilises and combines with the carbon, forming disulphide of carbon, which passes off in vapour and condenses in the liquid form at the bottom of the water. For larger quantities, a tubulated earthen retort is used, having a porcelain tube passing through the tubulus, and reaching nearly to the bottom. The retort is filled with charcoal, heated to redness in a furnace, and bits of sulphur dropt in through the tube. The neck of the retort is connected with a condensing tube kept cold by a stream of water, and passing into a receiver containing cold water as above described. The sulphide of carbon which collects at the bottom of the water is not pure, but contains excess of sulphur. It is purified by distillation at the heat of the water-bath, the sulphide of carbon then volatilising and the sulphur remaining behind.

Properties.—Disulphide of carbon is a colourless, very mobile, strongly refracting liquid, having a faint and peculiarly unpleasant odour. Its refracting power is 1·645. Specific gravity 1·293 at 0° C., and 1·271 at 15°. Boils at 46·6° under ordinary pressure, and evaporates quickly at ordinary temperatures, producing great cold. Vapour-density = 2·67, corresponding to 2 vols. $\left(\frac{12 + 2\,.\,32}{2} \times 0{\cdot}0623 = 2{\cdot}63\right)$. It is insoluble in *water*, to which, however, it imparts its odour. *Alcohol* and *ether* mix with it in all proportions. It dissolves *sulphur*, *phosphorus*, and *iodine;* sulphur and phosphorus separate from it by spontaneous evaporation in well defined crystals. It dissolves *camphor* and mixes easily with *oils*, both fixed and volatile.

Decompositions.—1. Disulphide of carbon is very inflammable, and burns with a blue flame, producing sulphurous and carbonic anhydrides.—2. The vapour passed over various *metallic oxides* at a red heat, yields the same gaseous products, together with a metallic sulphide; the sulphides thus formed are generally crystallised, and resemble those found in nature. Sulphide of carbon is indeed one of the most powerful sulphurising agents known, affording the means of producing several metallic sulphides not otherwise obtainable (Frémy). It likewise converts oxides into sulphides when heated with them in sealed tubes; with *water* at 150° C. it yields carbonic anhydride and sulphydric acid (Schlagdenhauffen, J. Pharm. [3] xxix. 401).—3. The vapour is strongly attacked by *nitric acid*, yielding sulphuric acid and nitrous vapours. —4. Sulphide of carbon heated with *chlorates* or *hypochlorites* reduces them to chlorides, with evolution of carbonic anhydride and deposition of sulphur.—5. Heated with aqueous *iodic acid* in a sealed tube, it yields hydriodic acid, together with free iodine and a deposit of sulphur, also sulphuric acid, sulphydric acid, and carbonic anhydride. Two reactions appear to go on at once, viz.:

$$2HIO^3 + CS^2 = I^2 + CO^2 + H^2SO^4 + S.$$
$$2HIO^3 + 2CS^2 + 2H^2O = 2CO^2 + 2HI + H^2SO^4 + H^2S + S^2.$$

The liquid is at first coloured violet by the free iodine, but on increasing the heat, the colour disappears, in consequence of the action of the sulphydric acid on the iodine, which produces hydriodic acid and free sulphur, the latter imparting a straw-yellow colour to the liquid (Pelouze and Frémy).—6. *Bromic acid* acts in like manner.—7. Many *metals* decompose disulphide of carbon at a red-heat, taking up the sulphur and setting the carbon free.—8. A mixture of sulphide of carbon vapour and *sulphydric acid gas* passed over *red-hot copper* yields sulphide of copper and marsh-gas (Berthelot):

$$CS^2 + 2H^2S + Cu^8 = 4Cu^2S + CH^4.$$

9. With *nascent hydrogen*, sulphide of carbon yields sulphydric acid, a crystallised body, CH^2S, and an oily substance not yet examined (Girard, Compt. rend. xliii. 39). —10. Dry *chlorine* converts it at a red heat into tetrachloride of carbon; at ordinary temperatures, into sulphochloride of carbon, $CSCl^2$; but with moist chlorine it yields trichloromethylsulphurous acid (the so-called sulphite of tetrachloride of carbon, $CCl^4SO^2 = SO^2.CCl^4$ (Kolbe).—11. *Bromine* and sulphide of carbon do not act upon each other when passed through a red-hot tube.—12. The *fixed caustic alkalis* gradually dissolve disulphide of carbon, forming a brown solution, which is a mixture of carbonate and sulphocarbonate of the alkali-metal (Zeise):

$$3CS^2 + 3K^2O = K^2CO^3 + 2K^2CS^3.$$

13. With *alcoholic potash* it yields carbonate and ethyl-oxysulphocarbonate (xanthate) of potassium, which forms a yellow precipitate with copper-salts (Zeise):

$$CS^2 + C^2H^5.K.O = \left.\begin{matrix}(CO)'' \\ C^2H^5.K\end{matrix}\right\}S^2.$$

An aqueous or alcoholic solution of caustic potash, boiled with disulphide of carbon, forms with lead-salts a black precipitate of sulphide of lead, which affords a very delicate test for sulphide of carbon. It is instantly produced on dropping a dilute solution of that compound into a boiling solution of nitrate of lead containing potash, a distinct coloration being obtained, even with a liquid containing only a drop of sulphide of carbon in a quart of water.—14. With *aqueous ammonia*, it forms sulphocarbonate and sulphocyanate of ammonium, without any carbonate (Zeise):

$$2CS^2 + 4NH^3 = (NH^4)^2CS^3 + NH^4.CNS.$$

15. With a saturated solution of *ammonia-gas in anhydrous alcohol*, it yields the same products, together with sulphocarbamate of ammonium, produced by the simple union of ammonia with the disulphide (Zeise):

$$CS^2 + 2NH^3 = (NH^2\overset{''}{C}S).NH^4.S.$$

16. With *triethylphosphine* it unites directly, forming a compound $P(C^2H^5)^3.CS^2$, which crystallises in splendid ruby-coloured prisms. The reaction affords an extremely delicate test for the presence of either of the constituent substances, and is especially applicable to the detection of sulphide of carbon in coal-gas. When a stream of the gas, purified from sulphuretted hydrogen in the usual manner, is passed through a solution of triethylphosphine in ether, contained in a bulb apparatus, a red colour soon appears in the liquid, and when sufficient gas has been passed through the liquid to evaporate the ether, the bulb-apparatus is seen to be lined with a network of the red crystals. (A. W. Hofmann, Ann. Ch. Pharm. cxv. 296.)

The sulphocarbonates M^2CS^3, or $M^2S.CS^2$, bear to disulphide of carbon the same relation that the carbonates M^2CO^3 bear to carbonic anhydride. Moreover by treating sulphocarbonate of ammonium with dilute sulphuric or hydrochloric acid, an oily, very acid liquid is precipitated, consisting of sulphocarbonic acid, H^2CS^3.

PROTOSULPHIDE OF CARBON. CS.—As already observed, it is doubtful whether this compound, the analogue of carbonic oxide, has yet been obtained, though there can be no doubt as to the possibility of its existence. Baudrimont (Compt. rend. xliv. 1000), states that it is obtained tolerably pure by passing the vapour of the disulphide over red-hot spongy platinum or pumice, and washing the resulting gas with solutions of acetate of lead and cuprous chloride, to free it from sulphydric acid and carbonic oxide, resulting from the action of air and moisture remaining in the materials. The gas thus obtained is described as colourless, smelling somewhat like the disulphide, not liquefiable at the temperature of a mixture of ice and salt; soluble in its own bulk of water; decomposed by lime-water into sulphide of calcium, and a volume of carbonic oxide equal to its own: $Ca^2O + CS = Ca^2S + CO$; and yielding when exploded with oxygen, equal volumes of CO^2 and SO^2.

Baudrimont likewise obtained the protosulphide, but mixed with sulphydric acid and carbonic oxide, by passing the vapour of the disulphide over red-hot charcoal; by the action of sulphydric acid on carbonic oxide at a red heat ($CO + H^2S = H^2O + CS$), and by several other processes.

Playfair (Chem. Soc. Qu. J. xiii. 248) endeavoured to prepare the protosulphide by passing the vapour of the disulphide over red-hot pumice, but obtained nothing but a mixture of carbonic anhydride, carbonic oxide, sulphydric acid, and nitrogen, saturated with vapour of disulphide of carbon; he observed no deposition of sulphur in the red-hot tube, though Baudrimont states that it choked up the exit-tube of his apparatus. Playfair attributes the formation of these gases to air and moisture retained by the pumice, though it had been previously ignited, or introduced into the tube together with the disulphide. He is of opinion that Baudrimont's gas, which yielded by explosion with oxygen, equal volumes of SO^2 and CO^2, was a mixture of equal volumes of CO and vapour of CS^2, which at common temperatures, and under the diminished pressure existing in the eudiometer, would have sufficient tension to diffuse itself in vapour through the carbonic oxide.

In face of these contradictory results, the question as to the actual formation of protosulphide of carbon must for the present be considered as undecided.

CARBON, SULPHOCHLORIDE OF. $CSCl^2$.—This compound, the analogue of phosgene, was discovered by Kolbe (Ann. Ch. Pharm. xlv. 53), and is produced: 1. By the action of dry chlorine on disulphide of carbon at ordinary temperatures, chloride of sulphur being formed at the same time: $CS^2 + Cl^4 = SCl^2 + CSCl^2$. A few grammes of the disulphide are left exposed for a few days to the action of perfectly dry chlorine in a closed flask, either in the dark or in sunshine; the resulting liquid is digested with water to decompose the chloride of sulphur, and the remaining oily liquid is freed from the acid products thereby formed, by repeated distillation with water and a small quantity of magnesia. It is essential to the production of this compound, that the materials be perfectly dry, as if moisture is present, another compound, trichloro-methyl-sulphurous acid is obtained (p. 776). At a red heat, a different action takes place, and tetrachloride of carbon is produced.—2. By passing a mixture of sulphydric acid and vapour of tetrachloride of carbon through a tube kept at a moderate red heat: $CCl^4 + H^2S = 2HCl + CSCl^2$.

Sulphochloride of carbon is a yellow liquid, not miscible with water, having a peculiar and powerful odour, very irritating to the eyes. Specific gravity 1·46. Boiling point 70° C. These numbers probably require correction, as it is very difficult to obtain the compound free from sulphide of carbon. It is not decomposed by water or acids, not even by fuming nitric acid. Caustic potash decomposes it slowly, forming carbonate and sulphide of potassium, and tetrachloride of carbon:

$$2CSCl^2 + 3K^2O = K^2CO^3 + 2K^2S + CCl^4.$$

CARBONATES. The carbonates form a numerous and important class of salts, many of which occur as natural minerals. They are usually divided into *normal*, *basic*, and *acid* carbonates, the normal or neutral salts having the composition

$$M^2CO^3 = M^2O.CO^2 = \left.\begin{matrix}(CO)''\\ M^2\end{matrix}\right\}O^3 \text{ [or } \mathit{MO.CO^2}\text{]}.$$

The basic carbonates, however, all contain water, and by regarding the whole or part of this water (or hydrogen) as basic, the carbonates, like the borates, phosphates, and silicates, may be divided into ortho-carbonates, $M^4CO^4 = \left.\begin{matrix}\overset{''''}{C}\\ M^4\end{matrix}\right\}O^4$, and metacarbonates, M^2CO^3,—or more generally orthocarbonates $= M^xH^{4n-x}C^nO^{4n}$, and metacarbonates $= M^xH^{2n-x}C^nO^{3n}$, the latter including the salts usually regarded as neutral carbonates. Nearly all the precipitates obtained by adding a solution of an alkaline carbonate to a salt of a heavy metal, contain water, and may be represented by one or other of these formulæ. It is difficult to say whether the ortho- or the meta-carbonates are the more numerous; but the carbonates of the stronger bases, viz. the alkali-metals and alkaline-earth metals, are certainly meta-carbonates. Only a few acid carbonates are known as definite salts, viz. those of potassium, sodium, and ammonium, and these are metacarbonates containing hydrogen, *e.g.* monopotassic metacarbonate, or diacid carbonate of potassium, $(KH)CO^3$.

Carbonates are formed by the action of carbonic acid, or the joint action of water and carbonic anhydride, on metallic oxides or hydrates, not in any case by the union of carbonic anhydride with an oxide without the intervention of water. Lime-water, or milk of lime, absorbs carbonic anhydride rapidly, forming carbonate of calcium; but perfectly dry carbonic anhydride may be passed over anhydrous lime without absorption. Even dry hydrate of potassium, KHO, absorbs carbonic anhydride but slowly, and soon becomes covered with a crust of acid carbonate of potassium ($KHO + CO^2 = KHCO^3$), which protects the rest from alteration; but the moist hydrate, or the aqueous solution, absorbs it with the greatest avidity; similarly with other bases. The carbonates of the earth-metals proper and heavy metals are most easily obtained by precipitating a soluble salt of the metal with an alkaline carbonate; but the precipitate, as already observed, almost always contains water, and very rarely has the composition of an anhydrous metacarbonate M^2CO^3. The sesquioxides, alumina, ferric oxide, chromic oxide, uranic oxide, &c., do not absorb carbonic anhydride even when moist, and their solutions, when mixed with alkaline carbonates, yield precipitates, not of carbonates, but of hydrates. Metals like zinc and iron, which readily replace hydrogen in acid solutions, may be converted into carbonates by simply immersing them in water containing carbonic acid.

Carbonates are also formed in the decomposition by heat of organic salts of the stronger bases, viz. of the alkali-metals and of the alkaline-earth metals. Oxalates are resolved into carbonates and carbonic oxide, without separation of carbon:

$$C^2M^2O^4 = CM^2O^3 + CO$$

formates into carbonates, with evolution of carbonic oxide and hydrogen, and slight separation of carbon:

$$2CHMO^4 = CM^2O^3 + CO + H^2.$$

The salts of most other organic acids yield a considerable quantity of free carbon besides combustible gases; acetates and the salts of other fatty acids, and a few others, are resolved by dry distillation into carbonates and acetones (pp. 31, 32).

The carbonates of ammonium, potassium, and sodium are easily soluble in water; carbonate of lithium dissolves in about 100 pts. of water; the carbonates of all other metals are insoluble, or nearly so, in water; but all are slightly soluble in water containing free carbonic acid. Acid carbonates are doubtless formed in this case; but none of these, excepting the acid carbonates of the alkali-metals, can be obtained in the solid state, as the solutions, when boiled or evaporated, give off carbonic anhydride and deposit neutral carbonate. All metallic carbonates, excepting carbonate of ammonium, are insoluble in alcohol. Carbonates of organic alkalis are for the most part soluble in water and in alcohol; carbonates of alcohol-radicles, insoluble in water, soluble in alcohol.

Most carbonates are easily decomposed by heat. The carbonates of the heavy metals are all decomposed at a low red heat, giving off carbonic anhydride, and leaving a residue of metal or of oxide. The carbonates of the earth-metals proper, and of calcium and strontium, require a stronger red heat to decompose them; carbonate of barium is decomposed only at a white heat; and the carbonates of the alkali-metals, when dry, resist the action of the strongest heat, excepting when a current of dry air or other gas is passed over them; in that case carbonate of sodium gives up a small quantity of carbonic anhydride, and carbonate of lithium a considerable quantity. (H. Rose.)

Nearly all carbonates are more or less decomposed by water, with the aid of heat, those of the weaker bases even at ordinary temperatures, so that precipitated carbonates are very apt to undergo partial decomposition during washing. Even the carbonates of barium, potassium, sodium, and magnesium are converted into hydrates when heated to redness in a stream of aqueous vapour; partially also in a stream of moist air or hydrogen gas: the carbonates of barium and potassium do not suffer any decomposition in a current of dry air or hydrogen. (H. Rose, Pogg. Ann. lxxxv. 99, 279; Jahresber. f. Chem. 1852, p. 309.)

Carbonates are decomposed, with evolution of carbonic anhydride, by nearly all acids, even at ordinary temperatures, and at a red heat by many acids whose salts are themselves decomposed at ordinary temperatures by carbonic acid, *e.g.* by boric, silicic, and several metallic acids. The effervescence which accompanies the decomposition affords a ready indication of the presence of a carbonate. Any of the stronger acids may be used to effect the decomposition, but, generally speaking, hydrochloric or nitric acid is preferable to sulphuric acid, because the latter often forms insoluble or sparingly soluble salts, the presence of which interferes with the reaction. If the carbonate is in solution, the liquid should be concentrated before adding the acid, as in a very dilute liquid the carbonic acid may remain dissolved instead of escaping as gas. The decomposing acid must also be added in excess, otherwise an acid carbonate of the alkali-metal will be formed, and no effervescence will be observed. If the substance to be examined is a mineral, it must be finely pulverised, and the powder should be soaked in water before adding the acid; otherwise the escape of air-bubbles might be mistaken for an evolution of carbonic anhydride. Many other volatile acids produce effervescence when eliminated from these compounds, *e.g.* hydrochloric, hydriodic, sulphurous, sulphydric acid, &c.; but they may all be distinguished from carbonic acid by their colour or their odour, also by passing the evolved gas into lime-water or baryta-water, and proceeding as described at page 768.

CARBONATE OF ALUMINIUM (?) It is doubtful whether such a compound exists. Saussure stated long ago that alkaline carbonates throw down from solutions of aluminium, a compound of hydrate of aluminium with a small quantity of the alkaline carbonate, and that the hydrate is partially soluble in aqueous carbonic acid, but is completely separated on warming the solution or exposing it to the air (Gm. iii. 309). Other chemists have, however, obtained different results. According to **Muspratt** (Chem. Soc. Qu. J. ii. 206), the precipitate formed by alkaline carbonates consists of $3Al^4O^6.2CO^2 + 16H^2O$. **Langlois** (Ann. Ch. Phys. [3] xlviii. 502) found $8Al^4O^3.3CO^2 + 40H^2O$; and **Wallace** (Chem. Gaz. 1858, 410) gives, as the composition of the precipitate, $3Al^4O^3.2CO^2 + 9H^2O$. **H. Rose**, on the contrary (Pogg. Ann. xli. 462), states that the precipitate formed by carbonate of ammonium is a compound of trihydrate of aluminium with carbonate of ammonium, $Al^2H^3O^3 + NH^4.H.CO^3$, the ammonia-salt not being removable by washing. From experiments recently made in Dr. Muspratt's laboratory by Mr. **James Barratt** (Chem. News, i. 110), it appears that the precipitate formed by carbonate of sodium in a solution of chloride of aluminium, after being washed and dried, then triturated with water, again washed, and dried over sulphuric acid, consists of pure hydrate of aluminium.

CARBONATE OF ALLYL. See CARBONIC ETHERS.

CARBONATES OF AMMONIUM. These salts have already been described (p. 190). They are all metacarbonates, and may be formulated as follows:

Neutral carbonate, $(NH^4)^2O.CO^2 \quad = \quad \left.\begin{matrix}\overset{\prime\prime}{C}O\\(NH^4)^2\end{matrix}\right\}O^2$

Acid carbonate, $\left.\begin{matrix}NH^4\\H\end{matrix}\right\}O.CO^2 \quad = \quad \left.\begin{matrix}\overset{\prime\prime}{C}O\\NH^4.H\end{matrix}\right\}O^2$

Sesquicarbonate, $2(NH^4)^2O.3CO^2 + 3aq. = \left.\begin{matrix}(\overset{\prime\prime}{C}O)^3\\(NH^4)^4.H^2\end{matrix}\right\}O^6 + aq.$

CARBONATE OF AMYL. See CARBONIC ETHERS.

CARBONATE OF BARIUM. $Ba^2CO^3 = Ba^2O.CO^2$.—This salt occurs abundantly in nature as *Witherite*, a mineral which frequently accompanies lead-ores. It crystallises in the trimetric system, isomorphously with arragonite, the crystals being frequently prismatic, from predominance of the faces ∞P, $\infty \breve{P} \infty$, and $\breve{P} \infty$. The combination $P \,.\, 2\breve{P} \infty \,.\, \infty \breve{P} \infty \,.\, \infty P$, is also common, forming a six-sided prism with pyramidal summits. Ratio of axes, $a : b : c = 0.5950 : 1 : 0.7413$. Inclination of faces: $\infty P : \infty P = 61° 30'$; $\breve{P} \infty : \breve{P} \infty = 71° 47'$; $2\breve{P} \infty : 2P \infty = 110° 42'$. Cleavage imperfect parallel to $\infty \breve{P} \infty$, ∞P, and $\breve{P} \infty$ (Kopp). It occurs also in globular, tuberose, and botryoïdal forms; structure either columnar or granular; also amorphous. Specific gravity = 4·29 to 4·35. Hardness = 3 to 3·75. Lustre vitreous, inclining to resinous on fractured surfaces. Colour white, or often yellowish or greyish. Streak white. Subtransparent to translucent. Fracture uneven. Brittle. Witherite is found on Alston Moor in Cumberland, and in splendid crystals at Fallowfield in Northumberland. It occurs also in many places on the continent of Europe, in the Altai, near Coquimbo, Chili, &c. It is sometimes found altered to heavy spar by the action of soluble sulphates.

Carbonate of barium is rapidly formed when baryta, either in the anhydrous state, or in crystals, or in solution, is exposed to the air, and is easily prepared by precipitating an aqueous solution of the chloride or nitrate with carbonate of ammonium, or a solution of the sulphide with carbonate of sodium; the salt obtained by this last method is liable to be contaminated with a sulphur-compound. It may also be prepared in an impure state by igniting in a crucible a mixture of 10 pts. of native sulphate of barium, 2 pts. of charcoal, and 5 pts. of carbonate of potassium (pearl-ash). A mixture of sulphide of potassium and carbonate of barium is then obtained, from which the sulphide of potassium may be extracted by water. The impure carbonate thus produced may be used for the preparation of other barium-salts, but the salts thus obtained will contain iron.

Carbonate of barium artificially prepared is a soft white powder. It is poisonous, and is used as rat-bane. It is very slightly soluble in water, about 1 pt. in 4000, rather more (in 588 pts. according to Lassaigne) in water saturated with carbonic acid. It dissolves easily, even in the cold, in chloride, nitrate, and succinate of ammonium, and when boiled with chloride of ammonium, it is completely decomposed, yielding carbonate of ammonium and chloride of barium. When shaken up with aqueous sulphate of potassium or sodium, it yields sulphate of barium and carbonate of the alkali-metal. It bears a strong red heat without decomposition; but at the heat of a forge-fire it gives off carbonic anhydride and leaves baryta. The decomposition is greatly facilitated by the addition of charcoal. Carbonate of barium is decomposed by vapour of water at a red heat, and very easily if mixed with an equal weight of chalk or slaked lime.

An *acid carbonate*, $2Ba^2O.3CO^2$, or $2Ba^2CO^3.CO^2$, was said by Boussingault (Ann. Ch. Phys. [2] xxix. 280) to be obtained by precipitating chloride of barium with sesquicarbonate of sodium. H. Rose, on the other hand, by mixing chloride of barium with diacid carbonate of sodium or potassium, obtained nothing but neutral carbonate of barium, and is of opinion that acid carbonates of barium cannot exist excepting in solution.

CARBONATE OF BISMUTH.—When nitrate of bismuth is dropt into a solution of alkaline carbonate, a white precipitate is formed, consisting of $Bi^2O^3.CO^2$ (Berzelius). The precipitate formed with alkaline carbonates contains $Bi^2O^3.CO^2 + \frac{1}{2}aq.$, the water escaping at 100° C. (Lefort.)

CARBONATE OF CADMIUM, Cd^2CO^3, occurs in small quantity, associated with native carbonate of zinc. Cadmium-salts yield with carbonate of ammonium, a white precipitate, containing $Cd^2CO^3 + aq.$, which gives off its water between 80° and 120° C.; at a higher temperature, carbonic anhydride goes off, and brown oxide of cadmium is left, which when exposed to the air is gradually reconverted into carbonate (Lefort, J. Pharm. [3] xii. 406). According to H. Rose (Pogg. Ann. lxxxv. 304), the precipitates formed by alkaline carbonates in solutions of cadmium, contain very little water, and approach very nearly to the formula Cd^2CO^3. Moist hydrate of cadmium absorbs carbonic acid from the air, and at 300° gives off all its water, and is converted into $2Cd^2O.Cd^2CO^3$, or $Cd^2O.Cd^4CO^4$.

CARBONATES OF CALCIUM.—The *metacarbonate*, $Ca^2CO^3 = Ca^2O.CO^2$, occurs most abundantly in all parts of the world, in the forms of calcspar, marble, limestone of various kinds, and chalk; also in egg-shells and the shells of molluscs, and, together with phosphate of calcium, in bones. It is formed when lime, either anhydrous or hydrated, is exposed to the air in its ordinary state of moisture, but not by the action of carbonic anhydride on anhydrous lime. It may be obtained pure by dissolving calcined oyster shells, chalk, or marble, in hydrochloric acid, adding ammonia or milk of lime to precipitate alumina, oxide of iron, and earthy phosphates, then filtering, precipitating the hot filtrate with carbonate of ammonium, washing thoroughly, and drying at a heat short of redness.

Carbonate of calcium is dimorphous, crystallising in the hexagonal system as calcspar (p. 721), and in the trimetric system as arragonite (p. 358). The specific gravity of the former varies from 2·6987 to 2·75; of the latter, generally from 2·92 to 3·28. The artificially prepared salt is a white powder, consisting of small crystals, which usually take the form of arragonite when precipitated from hot solutions, and of calcspar when precipitated from cold solutions, especially if dilute. The microscopic crystals of arragonite gradually change into rhombohedrons of calcspar if left for some time under the cold liquid (p. 359). The precipitate formed in hot solutions, assumes the crystalline character at once; that from cold solutions is amorphous at first, and gradually becomes crystalline.

Carbonate of calcium is tasteless, and has a slight alkaline reaction to test-paper. It is very sparingly soluble in water, requiring, according to Fresenius (Ann. Ch. Pharm. lix. 117), 88·34 pts. of boiling, and 10,601 pts. of cold water to dissolve it; the solution is slightly alkaline. Water containing free carbonic acid dissolves it much more freely. When recently precipitated, it dissolves easily in aqueous carbonate, sulphate, hydrochlorate, nitrate, or succinate of ammonium: but when it has assumed the crystalline form by long standing, it dissolves but sparingly, forming a turbid liquid. The clear solutions sometimes become turbid on standing, but do not deposit the whole of the calcium which they contain. Hence calcium can never be completely precipitated as carbonate from solutions containing ammoniacal salts. Carbonate of calcium boiled with solution of sal-ammoniac, the water being renewed as it evaporates, dissolves almost completely as chloride of calcium, with evolution of carbonate of ammonium.

Carbonate of calcium heated to full redness in open vessels, is resolved into lime and carbonic anhydride. The decomposition commences even at a low red heat, so that in estimating calcium as carbonate in analysis, the ignited precipitate should, before weighing, be moistened with carbonate of ammonium, and again heated, just sufficiently to drive off the excess of that salt; by this means, any carbonic acid that may have been driven off will be restored. In a current of air or any other gas, and especially of steam, the decomposition takes place at a lower temperature. If, on the other hand, the carbonate of calcium be ignited a closed iron tube, so that the carbonic anhydride cannot escape, it fuses to a fine-grained mass, consisting of crystals of calcspar, and having the appearance of marble.

Hydrated Neutral Carbonate of Calcium, Hydrocalcite, $Ca^2CO^3.5aq$.—This salt is obtained in small, very acute, rhombohedral crystals, of specific gravity 1·783, by boiling lime in a concentrated solution of sugar, milk-sugar, starch, or gum, and leaving the solution for some months in a cold place (Pelouze, Ann. Ch. Phys. [2] xlviii. 301). Becquerel, by exposing a solution of lime in sugar-water, to the action of a 12-pair voltaic battery, obtained crystals having the same composition, but the form of a rhombic prism with dihedral summits, like arragonite. Crystals of the same form and composition were found by Scheerer (Pogg. Ann. lviii. 382), in a running stream. Salm-Horstmar found six-sided prisms of the same composition, deposited from spring-water in the copper tube of a pump.

The crystals remain unaltered below 19° or 20° C., either in the air or under water, but crumble to a white powder at a somewhat higher temperature, and if quickly heated to 30°, they are converted into a pasty mass, which dries up to a powder. In ether at 30°, they crumble to a white powder; also in hydrated alcohol: but boiling absolute alcohol extracts from them only 2 at. water, rendering them opaque, but without change of form. The remaining crystals with 3 at. water, effloresce very quickly in the air, but may be kept unaltered at a temperature below 10°. (Gm. iii. 188.)

Orthocarbonate, Ca^4CO^4, or $2Ca^2O.CO^2$.—This, with 1 at. water (sometimes regarded as a hydrocarbonate, $Ca^2CO^3.2CaHO$), is, according to Fuchs (Pogg. Ann. xxvii. 601), the composition of the slaked lime produced by exposing quick lime to the air in its ordinary state. At a strong red heat, it gives off water and carbonic anhydride, and yields a quick lime which slakes in water, not with violence, but slowly and with only moderate rise of temperature. At a low red heat, the hydrated orthocarbonate gives off only water, leaving the anhydrous salt, Ca^4CO^4, which, according to Fuchs, is likewise produced when ordinary carbonate of calcium is exposed to a moderate red heat, only half of the carbonic anhydride being then expelled, and leaving a residue, which in contact with water does not slake but hardens, being in fact converted into the hydrated orthocarbonate.

Acid Carbonate.—This salt, which perhaps has the composition $CaHCO^3$, is known only in solution, and may be obtained in that state by passing carbonic anhydride into cold water in which the neutral carbonate is suspended. Water saturated with carbonic acid dissolves $\frac{1}{1428}$ part of the neutral carbonate, at 0° C., and $\frac{1}{1136}$ at 10° (Lassaigne, J. Chim. méd. 1848, p. 312). In consequence of this sparing solubility, solutions of calcium-salts are precipitated by alkaline bicarbonates even in the cold. The solution of the acid salt has a slight alkaline reaction if quite saturated, but if the carbonic acid is in excess, it exhibits an acid reaction. It is decomposed, with separation of the neutral carbonate, on exposure to the air, or more quickly when heated. It plays an important part in the economy of nature, being formed wherever carbonate of calcium or other calcareous formations, especially silicates, come in contact with water containing carbonic acid, and thus entering in greater or smaller quantity into the composition of almost all natural waters. Waters which contain it in considerable quantity, form deposits of carbonate of calcium on their banks or on objects immersed in them; hence the formation of calcareous petrifactions, of calcareous tufa and sinter, of stalactites, stalagmites, &c. To the same cause also is due the turbidity which appears in river or spring water when heated, and the incrustation or furring of kettles and boilers. The formation of this incrustation may to a certain extent be prevented, by the addition of sal-ammoniac to the water, whereby, as already observed, the carbonate of calcium is converted into soluble chloride.

Carbonate of Cerium, $Ca^2CO^3 + 3aq.$, or $Ce^2H^2CO^4 + 2aq.$, formed, on exposing hydrated cerous oxide to the air, or by precipitation, is a white powder, which when ignited the air, is partly converted into lemon-yellow coroso-ceric oxide. It occurs native, with fluoride of calcium, as *Parisite* (*q. v.*)

Chromous Carbonate, is obtained by adding a solution of protochloride of chromium to carbonate of potassium. The precipitate is red or reddish-brown, if the solution is hot, but has the form of dense yellow or bluish-green flakes, if the solution is cold: it appears, however, to have the same composition in all cases. (Moberg.)

Carbonates of Cobalt. The anhydrous carbonate Co^2CO^3, is obtained by heating chloride of cobalt with carbonate of calcium to 150° C. in a sealed tube for eighteen hours, or by decomposing the chloride with a solution of acid carbonate of sodium supersaturated with carbonic acid, and heated to 140° in a strong vessel closed with a cork, through which the carbonic acid escapes slowly. It is a light rose-coloured, sandy powder, composed of microscopic rhombohedrons, and is not attacked in the cold by acids, not even by nitric or hydrochloric acid. (Sénarmont, Ann. Ch. Phys. [3] xxx. 129.)

The precipitates formed by adding cobalt-solutions to alkaline carbonates, are all hydrated carbonates, or double carbonates of cobalt and the alkali-metal. The former may be represented as ortho- or meta-carbonates, combined in various proportions with hydrate of cobalt, the composition varying according to the temperature and concentration of the solutions.

The precipitate formed on adding sulphate of cobalt to neutral carbonate of sodium, the solutions being concentrated or moderately dilute, and either hot or cold, is rose-coloured, and when dried at 100° C., consists of $Co^2CO^3.3CoHO + \frac{1}{2}aq.$, or $Co^4CO^4.CoHO + \frac{3}{2}aq.$ (Setterberg, Pogg. Ann. xix. 55; Winkelblech, Ann. Ch. Pharm. xiii. 148; H. Rose, *ibid.* lxxx. 237). But very weak solutions mixed at the boiling heat, yield a blue precipitate, consisting of $Co^2CO^4.4CoHO + aq.$, or $Co^4CO^4.2CoHO + 2aq.$ The precipitates are very difficult to wash. Heated above 150° C. in contact with the air, they gradually give off water and carbonic anhydride, and are converted into sesquioxide of cobalt (H. Rose). The first-mentioned precipitate is partly converted into sesquioxide by boiling with water (Field, Chem. Soc. Qu. J. xiv. 50). The same precipitate digested with solution of diacid carbonate of sodium or of ammonium, is gradually converted into $3Co^2CO^3 + aq.$ (H. Deville, Ann. Ch. Phys. [3] xxxiii. 75.)

A hydrated carbonate of cobalt called *Remingtonite*, whose precise composition is not known, occurs as a soft, earthy, rose-coloured incrustation, on thin veins of serpentine, at a copper-mine near Finksburg, Carroll County, Maryland. (J. C. Booth, Sill. Am. J. [2] xv. 48.)

Carbonate of Cobalt and Potassium.—Nitrate or sulphate of cobalt forms with excess of diacid carbonate of potassium a rose-coloured precipitate, which gradually changes to a network of rose-coloured crystals, easily decomposed by water, and consisting of a meta-carbonate, $(Co^2KH)C^2O^6 + 4aq.$, [or $2(CoO.CO^2) + KO.2CO^2 + 9HO$](H. Rose, H. Deville). Nitrate of cobalt and sesquicarbonate of potassium, yield distinct crystals, containing $CoKCO^3 + 2aq.$ (Deville.)

Carbonate of Cobalt and Sodium.—Nitrate of cobalt and sesquicarbonate of sodium, yield a mixture of small prismatic crystals, $CoNaCO^3 + 2aq.$, and dark-red crystals, apparently cube-like rhombohedrons, containing $CoNaCO^3 + 5aq.$ (Deville).

Carbonates of Copper.—Two of these compounds occur as natural minerals, viz. *Malachite* and *Azurite*. They may be most simply represented as orthocarbonates, viz.:

Malachite as *tetracupric orthocarbonate*, $Cu^4CO^4 + aq.$

Azurite as *tricupric orthocarbonate*, $\left.\begin{matrix}Cu^3\\H\end{matrix}\right\}CO^4$.

They may also be regarded as metacarbonates combined with cupric hydrate, viz. malachite as $Cu^2CO^3.2CuHO$; azurite as $Cu^2CO^3.CuHO$. The hydrated tetracupric salt is formed artificially by precipitation. The anhydrous metacarbonate Cu^2CO^3, is not known.

Tetracupric Orthocarbonate, $Cu^4CO^4 + aq.$ *Malachite, Green Carbonate of Copper, Mountain green, Atlas ore.*—This mineral forms prismatic crystals belonging to the monoclinic system, in which the lengths of the orthodiagonal, clinodiagonal, and principal axis are to one another as 1·273 : 1 : 0·5358. The inclination of the clinodiagonal to the principal axis does not differ much from 90°. The crystals are generally reduced to thin prisms by predominance of the faces ∞P and $\infty P\infty$, and terminated by oP, $+P$, $-P\infty$. Cleavage perfect parallel to $-P\infty$ and ∞P (Kopp). More frequently, however, it occurs in laminar, fibrous, compact, or earthy masses. Specific gravity = 3·7 to 4·0. Hardness = 3·5 to 4. It varies in colour from emerald to grass-green, and exhibits all degrees of transparency down to perfect opacity. It takes a high polish, and when in large masses is cut into tables, snuff-boxes, vases, &c. Malachite usually accompanies other ores of copper. Perfect crystals are very rare. The fibrous variety occurs abundantly in Siberia, at Chessy in France, at Sandlodge in Shetland; the compact variety at Schwartz in the Tyrol, in Cornwall, and in Cumberland. At the copper mines of Nischne Tagilsk, a bed of malachite was opened which yielded many tons of the mineral. Malachite is also found on the west coast of Africa, and in several localities in North America. (Dana, ii. 458.)

Cupric salts treated with alkaline carbonates, yield at first a greenish-blue precipitate, consisting, according to Brunner, of $Cu^4CO^4 + 2aq.$; which, however, when left in contact with the liquid, and washed, becomes compact and green, and acquires the composition of malachite. When heated to 200° C. it is slowly converted into black cupric oxide, which obstinately retains a small quantity of water. Malachite slowly decomposes in the same manner at 220°. The tetracupric salt, either native or precipitated, is decomposed by boiling with water, giving up carbonic acid, and being entirely converted into black oxide of copper. (H. Rose; F. Field, Chem. Soc. Qu. J. xiv. 71.) By digestion with neutral carbonate of sodium at 120° F. (48·8° C.) it is converted into $6Cu^2O.CO^2$, or $Cu^4CO^4.4Cu^2O$. Boiled with sesquicarbonate of sodium, it dissolves, forming a blue liquid, which is not decomposed even by long boiling; but when sulphate of copper is boiled for a very long time with sesquicarbonate of sodium, a green precipitate of tetracupric carbonate is obtained, and on filtering from this and adding more sulphate of copper to the filtrate, the basic salt just mentioned is precipitated, as a dense black powder (Field). According to Deville, tetracupric carbonate digested with neutral carbonate of sodium, is partly converted into $8Cu^2O.CO^2 + 5H^2O$.

Anhydrous tetracupric carbonate, Cu^4CO^4, or $2Cu^2O.CO^2$, occurs, according to Thomson (*Mineralogy*, i. 601), as *mysorin*, a mineral from Mysore in Hindostan, containing also ferric oxide and silica. Dana suggests that it may be only an impure malachite.

Tricupric Orthocarbonate, Cu^3HCO^4 (or $3CuO.2CO^2 + aq.$) *Azurite, Lasurite, Blue Carbonate of Copper, Blue Malachite, Chessy Copper, Chessylite, Kupferlasur.*—This mineral occurs in fine crystals, belonging to the monoclinic system, in which the orthodiagonal, clinodiagonal, and principal axis are to one another as 1·181 : 1 : 2·076. Inclination of axes 87° 39′. Observed faces $\infty P . oP . [P\infty] . [\frac{1}{3}P\infty] . \infty P\infty$, together with others of less frequent occurrence. The crystals are often prismatically elongated in the direction of the orthodiagonal. Cleavage parallel to $[P\infty]$ (Kopp's *Krystallographie*, p. 303). The mineral occurs also massive and in imitative shapes, having a columnar composition, also dull and earthy. Specific gravity = 3·5 to 3·831. Hardness = 3·5 to 4·25. Lustre vitreous, almost adamantine. Colour, various shades of azure, passing into Prussian-blue. Streak-blue, lighter than the colour. Transparent to sub-translucent. Fracture conchoïdal. Brittle. It is found in splendid crystallisations at Chessy near Lyons, in fine crystals also in Siberia, at Moldavia in the Bannat, at Wheal Buller, near Redruth in Cornwall; at Porto Bello, South America; and in small quantities at Alston Moor, Wanlockhead, &c. It is found also in the States of Pennsylvania, New York, and New Jersey. (Dana, ii. 459.)

Azurite when ground to fine powder forms a bright blue pigment; but it is not of much use, as it is apt to turn green by exposure. When boiled with water, it decomposes like malachite, yielding black oxide of copper. Heated with a concentrated solution of diacid carbonate of sodium, it yields a blue solution, which, after protracted boiling, deposits a green precipitate of malachite (Field). According to Phillips (Ann. Ch. Phys. [2] vii. 44) a cupric carbonate, called *blue verditer*, having the same composition as azurite, is obtained by a secret process.

Potassio-cupric Carbonate.—Nitrate of copper forms with diacid carbonate of potassium, a deep blue liquid, which after a few hours deposits a silky mass, consisting of $5Cu^2O.K^2O.5CO^2 + 10$ aq. or $(Cu^{10}K^2H^8)C^5O^{20} + 6$ aq. (Deville, Ann. Ch. Phys. [3] xxxiii. 75).

Sodio-cupric Carbonate, $CuNaC^2O^3 + 3$ aq., is obtained by adding an acid solution of nitrate of copper to carbonate of potassium containing soda, and leaving the precipitate in the liquid for a considerable time; also by the action of diacid carbonate of sodium on tetracupric carbonate at 40°—50° C. It forms rhombic prisms, having the angles of the obtuse edges = 123° 14′, and acuminated with four faces resting on the prismatic edges. (Deville.)

Cuprous Carbonate?—The yellow precipitate obtained by adding carbonate of sodium to a solution of cuprous chloride in hydrochloric acid was said by Colin to be a cuprous carbonate, but according to L. Gmelin (*Handbook*, v. 414), it is merely cuprous hydrate.

Carbonate of Cuprammonium, $(NH^3Cu)^2CO^3$, is obtained in large deep blue crystals by dissolving tricupric or tetracupric carbonate in carbonate of ammonia, and pouring the solution into alcohol. It is rapidly decomposed by water into carbonate of ammonia and a basic carbonate of copper, $Cu^4CO^4.2CuHO + 2$ aq. (Favre, *Traité de Chimie par Pelouze et Frémy*, iii. 201). The same ammoniacal compound appears to be formed when cupric oxide or finely divided metallic copper is digested in ammonia with access of air.

CARBONATE OF DIDYMIUM is obtained as a white, slightly rose-coloured precipitate containing $Di^2CO^3 + 2$ aq., on adding an alkaline carbonate to the solution of a didymium-salt. At 100° C. it gives off two-thirds of its water and a small quantity of carbonic acid. (Marignac.)

CARBONATE OF ETHYL. See CARBONIC ETHERS.

CARBONATE OF GLUCINUM is produced when the hydrate is exposed to the air, also by precipitating glucinum-salts with alkaline carbonates, not in excess, and by boiling a solution of carbonate of glucinum and ammonium. It appears to vary in composition; the precipitate obtained by the last-mentioned process has, according to Schaffgotsch, the composition $5Gl^2O.CO^2 + 5$aq. or $Gl^4CO^4.6GlHO + 2$aq. It appears to be decomposed by boiling with water. It dissolves in alkaline carbonates, forming double salts.

Carbonate of Glucinum and Ammonium.—When a solution of glucina in aqueous carbonate of ammonia is heated to the boiling point, till the liquid begins to show turbidity, then filtered, and the filtrate mixed with alcohol till it becomes milky, white transparent crystals are gradually deposited, containing $4Gl^2O.3CO^2.H^2O + 3[(NH^4)^2O.CO^2]$ or perhaps $GlHO.3Gl(NH^4)CO^3$. They become dull on exposure to the air, are insoluble in absolute alcohol, but dissolve readily in cold water, and are decomposed by hot water, with evolution of carbonate of ammonia. (Debray, Ann. Ch. Phys. [3] xliv. 5.)

Carbonate of Glucinum and Potassium, $GlHO.3GlKCO^3$, is obtained in the same manner as the ammonium-salt, which it resembles in its properties. (Debray.)

Carbonate of glucinum likewise forms a double salt with carbonate of sodium.

CARBONATES OF IRON.—*Ferric carbonate* does not appear to exist. The precipitate formed by alkaline carbonates in solution of ferric nitrate, consists, according to L. Gmelin (*Handbook*, v. 222), of ferric hydrate without a trace of carbonic acid. According to Soubeiran (Ann. Ch. Phys. [2] xliv. 326), the precipitate thrown down by alkaline carbonates from ferrous salts, contains, after thorough washing and exposure in thin layers to the moist air of a cellar for six months, 71·4 per cent. ferric oxide (quite free from ferrous oxide), 8·3 carbonic anhydride, and 20·0 water; but it is doubtful whether a definite carbonate is formed.

Double carbonates of ferricum and the alkali-metals appear to be capable of existing in solution, though not in the solid state. When a ferric salt is precipitated by concentrated carbonate of ammonia, the precipitated ferric hydrate gradually redissolves, but is slowly deposited again on diluting with water. Well washed ferric hydrate, however, does not dissolve in carbonate of ammonia, so that the presence of the ammoniacal salt formed in the decomposition appears to be necessary to the solution of the ferric hydrate. Similar reactions are obtained with strong solutions of carbonate of potassium or sodium.

Ferrous Carbonate.—The anhydrous metacarbonate Fe^2CO^3 or $Fe^2O.CO^2$, exists abundantly as a natural mineral, viz. *Spathic* or *Sparry iron ore*, also called *Chaly-*

lite, Siderite, Siderose, Brown spar, Sphærosiderite, Junkerite, Strahlstein, Eisenspath, Spatheisenstein, Oligonspath. This mineral forms rhombohedral crystals, having for their primary form a rhombohedron, in which the principal axis is to the secondary axes as 0·8117 : 1, and the inclination of the faces meeting in the terminal edges = 107° 0′, this form being either solitary or predominant, and often with curved faces; sometimes in twin-crystals. It also occurs in botryoïdal and globular forms (as *sphærosiderite*), occasionally in silky fibrous masses; often cleavable massive, with cleavage planes undulate; also coarse or fine granular. Specific gravity = 3·7 to 3·9. Hardness = 3·5 to 4·5. Lustre vitreous to pearly. Streak white. Colour ash-grey, yellowish-grey, greenish-grey; also brown and brownish-red, rarely green; sometimes white. Translucent to subtranslucent. Fracture uneven. Brittle. (Dana, ii. 445.)

Pure ferrous carbonate would contain 37·93 per cent. carbonic anhydride and 62·07 ferrous oxide. The mineral always contains more or less of the carbonates of manganese, magnesium, and calcium. A black variety from Babbowsky gave 36·61 CO^2, 57·91 Fe^2O, 1·51 Mn^2O, trace of Mg^2O, 0·59 Ca^2O, and 0·60 gangue. A specimen from the neighbourhood of Durham yielded 35·90 CO^2, 54·57 Fe^2O, 1·15 Mn^2O, 3·18 Ca^2O, and 2·63 water (= 97·43). The variety called oligonspar contains 25·31 per cent. manganous oxide; other varieties contain 12 to 15 per cent. magnesia.

Ferrous carbonate is a very abundant mineral, occurring in gneiss, mica slate, clay slate, and in connection with the coal formation. At Freiberg it occurs in silver mines. In Cornwall it accompanies tin. It is also found accompanying copper and iron pyrites, galena, vitreous copper, &c. In New York, according to Beck, it is almost always associated with specular iron. Occasionally it is found in trap rocks as sphærosiderite (Dana). A siliceous or argillaceous variety called *clay iron stone*, which occurs in the coal measures, is one of the most abundant and valuable ores of iron. Very large quantities of it are found and worked in South Staffordshire, at Merthyr Tydvil in South Wales, and near Glasgow.

Anhydrous ferrous carbonate may be prepared artificially by processes similar to those already described for carbonate of cobalt (p. 782). It then forms a greyish-white crystalline sand, composed of minute rhombohedrons, scarcely attacked by dilute acids, nearly unalterable in dry air, gradually assuming a light red tint in moist air. It is of a darker grey colour and less alterable in the air in proportion as the heat employed in its preparation has been greater and longer continued. (Sénarmont, Ann. Ch. Phys. [3] xxx. 129.)

Hydrated ferrous carbonate is precipitated on mixing a ferrous salt with an alkaline carbonate, in thick white flakes, which, on exposure to the air, absorb oxygen and give off carbonic acid, first assuming a dirty green colour, and ultimately changing to yellowish-brown ferric hydrate. Hence it is difficult to obtain the precipitated ferrous carbonate in a pure and definite state. The best mode of proceeding is to precipitate ferrous sulphate quite free from ferric sulphate, with alkaline monocarbonate or bicarbonate, both salts being dissolved in water which has been thoroughly freed from air by boiling, wash the precipitate out of contact with the air, *e.g.* by decantation with thoroughly de-aërated water, keeping the vessel quite full and closed, and dry it in an atmosphere of carbonic anhydride. The salt thus prepared is a greenish tasteless powder, which is used in medicine; it is tolerably permanent if thoroughly dried; but if moist it oxidises quickly in the air, becoming hot, and giving off water and carbonic acid. It may be rendered more permanent by mixing it with sugar while moist.

Acid Salt.—Aqueous carbonic acid dissolves ferrous carbonate; also metallic iron with evolution of hydrogen. The solution, which exists in many natural waters, called *chalybeate waters*, is colourless, has a slightly ferruginous taste, is decomposed, with separation of ferric hydrate, by contact with the air, and gives a black precipitate with sulphuretted hydrogen. To preserve chalybeate water in vessels, they must first be filled with carbonic anhydride, then opened and filled below the surface of the water, and lastly corked under water. A less efficient mode of preservation is the introduction of iron wire and a few grains of sugar.

CARBONATE OF LANTHANUM, $La^2CO^3 + 3$ aq., is found native as *Lanthanite*, a mineral (formerly mistaken for carbonate of cerium) occurring in four-sided plates or minute tables of the trimetric system, with bevelled edges; also fine-granular, and earthy. Specific gravity 2·67 (?) Hardness 2·5 to 3. It has a dull or pearly lustre, and greyish-white, faint pink, or yellowish colour. It is found coating cerite at Bastnas in Sweden, and in silurian limestone, with the zinc ores of the Saucon valley, Lehigh county, Pennsylvania. The American mineral was found by J. L. Smith to contain 54·90 per cent. La^2O, with oxide of didymium, 22·58 CO^2, and 24·09 water (= 101·57), the formula requiring 52·94 La^2O, 21·11 CO^2, and 25·95 water. With borax or phosphorus-salt it yields a glass having an amethystine colour, arising from didymium. (Dana, ii. 456.)

Carbonate of lanthanum obtained by precipitation forms a white gelatinous mass, which gradually changes into shining crystalline scales.

Carbonates of Lead.—The anhydrous metacarbonate, Pb^2CO^3 or $Pb^2O.CO^2$, is found native as *white lead ore* or *cerusite*, in crystals of the trimetric system, isomorphous with arragonite, witherite, and strontianite, and in which the brachydiagonal, macrodiagonal, and principal axis are in the ratio of 0·6100 : 1 : 0·7236. Ordinary combination $P . \infty P . \breve{P}\infty . 2\breve{P}\infty . \infty P\infty$, with $2\breve{P}\infty$ predominant. Inclination of faces, $\infty P : \infty P = 62° 46'$; $\breve{P}\infty : \breve{P}\infty = 71° 47'$; $2\breve{P}\infty : 2\breve{P}\infty = 110° 42'$. Cleavage moderately easy parallel to ∞P, less so parallel to $2\breve{P}\infty$. It is sometimes found in twin-crystals, the face of combination being ∞P (Kopp's *Krystallographie*, p. 261); rarely fibrous; often granularly massive and compact. Specific gravity 6·465 to 6·480. Hardness 3 to 3·5, in some earthy varieties as low as 5·4. Colourless when pure, transparent or translucent in various degree and with adamantine lustre. Fracture conchoïdal. Very brittle. White lead ore is found in Cornwall and Cumberland, at Leadhills and Wanlockhead in Scotland, in Siberia, in the Harz, in Bohemia, and many other localities. It sometimes occurs altered to phosphate of lead by the action of water containing phosphate of calcium; to galena by the action of sulphuretted hydrogen, and to minium by oxidation; also more or less to magnesite, malachite, and chrysocolla. (Dana.)

Horn-lead or *cerasine* is a compound of carbonate and chloride of lead.

Hydrocarbonates.—The precipitate formed in solutions of lead-salts by alkaline carbonates varies in composition according to the temperature and concentration of the liquids. According to Berzelius, the anhydrous metacarbonate is obtained by treating nitrate of lead with excess of carbonate of ammonia; according to Lefort (J. Pharm. [3] xv. 26), by precipitating with alkaline carbonates in the cold, whereas from hot solutions a hydrated salt, $3Pb^2O.CO^2.H^2O$, is obtained. According to H. Rose (Ann. Ch. Pharm. lxxx. 235), the precipitate always contains hydrate of lead. Equivalent quantities of nitrate of lead and neutral carbonate of sodium in cold strong solutions yield the compound $6Pb^2CO^3.2PbHO + aq.$, which gives off some of its water at 100° C., and takes up more carbonic acid; with cold dilute, or hot concentrated solutions, the compound $5Pb^2CO^3.2PbHO$ is obtained, and with hot dilute solutions $3Pb^2CO^3.2PbHO$. When the carbonate of sodium is added in excess, the precipitate consists chiefly of $Pb^2CO^3.PbHO$ or $(Pb^3H)CO^4$, but contains a small quantity of soda.

Hydrated carbonates of lead are also formed by the direct action of carbonic acid on hydrate of lead, and the compounds thus obtained differ from the precipitated carbonate, in being amorphous and perfectly opaque, whereas the precipitated carbonate is an aggregate of minute transparent crystalline grains. Hence the carbonate formed by absorption of carbonic acid is much better adapted for a pigment, and is extensively used as such under the name of *white lead* or *ceruse*; its great opacity gives it that quality which painters call *body*, enabling a small quantity of it to form a brilliant white coating over a considerable surface.

There are two methods of prepared white lead. In the older, called the Dutch method, because it was originally practised in Holland, thin sheets of lead are placed over gallipots containing weak acetic acid (water with about 2½ per cent of the strong acid), the pots being embedded in fermenting tan, the temperature of which varies from 140° to 150° F. The action is often very rapid, the metal disappearing in a few weeks to the centre of the sheet. In this process from 2 to 2½ tons of lead (4480 to 5600 lbs. are converted into carbonate by a quantity of vinegar containing not more than 50 lbs. of strong acetic acid. It is evident, therefore, that the metal is neither oxidised nor carbonated at the expense of the acetic acid. The oxygen is derived from the air, and the carbonic acid from the fermenting tan; the acetic acid merely serves to dissolve the oxide of lead and convert it into a basic acetate, which is easily decomposed by carbonic acid, the acetic acid being thereby set free to act upon another portion of oxide of lead. That this is really the mode of action, is shown by what takes place in the more modern process, in which oxide of lead (litharge) is mixed with water and about 1 per cent. of neutral acetate of lead, and carbonic acid gas is passed over it: in this manner the oxide is quickly converted into excellent white lead. Nitrate of lead has also been used in this latter process in place of the acetate.

White lead is a mixture or compound of carbonate and hydrate of lead, in various proportions. Mulder (Ann. Ch. Pharm. xxxiii. 242), from the analysis of numerous samples, concluded that there are three varieties of it, viz.: $Pb^2CO^3.PbHO$; $5Pb^2CO^3.6PbHO$, and $3Pb^2CO^3.2PbHO$. J. A. Phillips (Chem. Soc. Qu. J. iv. 165) found the composition of four samples to agree with the first of these formulæ, one with the third, and another to contain $5Pb^2CO^3.2PbHO$.

White lead is often mixed with heavy spar and gypsum, the addition of which renders it less liable to be blackened by the action of sulphuretted hydrogen. Oxide of zinc is likewise added for the same purpose. (Gm. iv. 127. *Ure's Dictionary of Arts, Manufactures and Mines*, iii. 1015; *Graham's Chemistry*, 2nd edition, ii. 120.)

Acid Carbonate.—Carbonate of lead dissolves slightly in water containing carbonic acid; the solution contains from $\frac{1}{8000}$ to $\frac{1}{5000}$ of lead-oxide, is rendered turbid by alkaline carbonates, and coloured brown by sulphuretted hydrogen. (See LEAD.)

Carbonate of Lead and Sodium. $4Pb^2CO^3.Na^2CO^3$.—Produced, according to Berzelius (Pogg. Ann. xlvii. 199), when nitrate of lead is precipitated by carbonate of sodium, the precipitate boiled in the alkaline liquid, then washed and dried at 160° C.

CARBONATE OF LITHIUM, Li^2CO^3.—This salt, which is slightly soluble in water, exists in the waters of Carlsbad, Franzensbad, and others. It is prepared by dissolving an excess of carbonate of ammonia in a concentrated solution of chloride of lithium, and washing the resulting precipitate with alcohol; or by precipitating sulphate of lithium with acetate of barium, evaporating the filtrate, and decomposing the residual acetate of lithium by ignition. The salt melts at a low red heat, and solidifies to a vitreous mass on cooling. It is not decomposed by heat. It dissolves in 100 pts. of cold water (Vauquelin); in 130 pts. at 13° C., and in 128·5 pts. at 100° (Kremers Jahresber. d. Chem. 1856, p. 275). The saturated solution boils at 100° (Kremers *ibid.* p. 294). The solution is alkaline, and deposits the salt by slow evaporation, in small prisms. It decomposes the salts of ammonia, and gives up its carbonic acid to caustic baryta and lime.

Water saturated with carbonic acid dissolves carbonate of lithium more freely than pure water.

CARBONATES OF MAGNESIUM.—The anhydrous metacarbonate, Mg^2CO^3, or $Mg^2O.CO^2$, occurs native as *magnesite*, associated with serpentine and other magnesian rocks. It is found in rhombohedral crystals, isomorphous with calcspar. Ratio of the principal axis to the secondary axes = 0·8117 : 1. Angle of the terminal edges = 107° 25. Cleavage perfect parallel to the rhombohedral faces. It also occurs massive, granular, or fibrous, sometimes in radiating groups; also very compact. Specific gravity = 2·8 to 3. Hardness = 3·5 to 4·5. It is white, or with various shades of yellow, grey, and brown, has a vitreous or silky lustre, and exhibits all degrees of transparency, down to complete opacity. Fracture flat, conchoïdal. It is infusible before the blowpipe, and dissolves slowly and with little effervescence in acids. It occurs nearly pure, with only small quantities of water and the carbonates of iron, manganese, and calcium, in Moravia, Styria, Silesia, Piedmont, Spain, and at several localities in the United States. Carbonate of magnesium occurs also associated in various proportions with the carbonates of iron, manganese, and calcium, forming the minerals sphærosiderite, diallogite, dolomite, bitter spar, &c.

Anhydrous metacarbonate of magnesium cannot be prepared by precipitating a soluble magnesium-salt with an alkaline carbonate, as the precipitate thus formed always contains hydrate of magnesium; but by suspending the washed precipitate in water, passing carbonic acid gas through the liquid till the precipitate is dissolved, and evaporating the solution by heat, the anhydrous salt is obtained as a crystalline powder, which when examined by the microscope, exhibits the form of arragonite (H. Rose, Pogg. Ann. xlii. 366). It is likewise obtained by heating sulphate of magnesium with carbonate of sodium, to 160° C. in a sealed tube, or by enclosing a soluble magnesium-salt, together with an alkaline dicarbonate supersaturated with carbonic acid, in a strong vessel closed by a cork, through which the carbonic acid can escape slowly. By this last method, it is obtained in microscopic rhombohedrons, like native magnesite (Sénarmont, Compt. rend. xxviii. 693; Ann. Ch. Phys. [3] xxx. 129). Anhydrous carbonate of magnesium is therefore isodimorphous with carbonate of calcium. When moistened with water, it gives an alkaline reaction with litmus and violets. If the solution of carbonate of magnesium in excess of carbonic acid be left to evaporate spontaneously, or kept for some time at 50° C., it deposits small hexagonal prisms, containing $Mg^2CO^3 + 3aq.$: they give up their water in warm air, becoming opaque, but retaining their form. The same hydrated crystals are obtained by mixing the solutions of sulphate of magnesium and sesquicarbonate of potassium and sodium, and leaving the mixture to stand. A saturated solution of carbonate of magnesium in aqueous carbonic acid, exposed for some time to a winter temperature, deposits transparent oblique prismatic crystals, containing 5 at. water: $Mg^2CO^3 + 5aq.$ They are converted into the preceding, with loss of transparency, by exposure to the air, more quickly in sunshine, and by immersion in water at 50° C. If boiled with water, they give up part of their carbonic acid, and are ultimately converted into $2Mg^2CO^3.MgHO + 2aq.$ (Fritzsche.)

Hydrocarbonates. a. $5Mg^2O.4CO^2 + 5aq. = 2Mg^2CO^3.MgHO + 2aq. = (Mg^5H^3)C^2O^6 + aq.$—Produced, as just mentioned, by the action of water on $Mg^2CO^3 + 5aq.$, better by boiling with water containing ammonia (Fritzsche); also by precipitating sulphate of magnesium with carbonate of sodium, and drying the precipitate at 100° C. (H. Rose, Ann. Ch. Pharm. lxxx. 234); also, according to Berzelius, by boiling a solution of acid carbonate of magnesium for a long time. It is a white granular powder.

b. $4Mg^2O.3CO^2 + 4aq. = 3Mg^2CO^3.2MgHO + 3aq. = (Mg^8H^4)C^3O^{12} + 2aq.$—Found native as *Hydromagnesite*, in small white, brittle, or acicular crystals, of the monoclinic system, or in chalky crusts. Specific gravity = 2·145 to 2·18. Hardness of the crystals = 3·5. It is found at Hrubschitz in Moravia in serpentine; in Negroponte near Kumi; and crystallised with serpentine and brucite (hydrate of magnesium), in Lancaster county, Pennsylvania. *Lancasterite* is a mixture of brucite and hydromagnesite. (Dana, ii. 456.)

A substance of the same composition is obtained by mixing sulphate of magnesium with excess of a hot solution of carbonate of potassium, and boiling the precipitate with fresh quantities of water, as long as any acid carbonate dissolves out (Berzelius); also, according to Fritzsche, by boiling a saturated solution of the acid carbonate, and twice boiling the resulting precipitate with fresh quantities of water. It is a white powder, slightly soluble in water, and forming an alkaline solution. When dried at 100° C. in the air, it absorbs carbonic acid, and is converted into $5Mg^2O.4CO^2 + 5aq.$ (H. Rose.)

c. $3Mg^2O.2CO^2 + 3aq.$ (?) Obtained, according to Fritzsche (Pogg. Ann. xxxvii. 310), by precipitating sulphate of magnesium with a very large excess of carbonate of sodium, boiling the whole till the precipitate passes from the flocculent to the granular condition; then washing and boiling rapidly with water, pouring off the liquid, and twice boiling the residue with fresh water. It consists of small grains mixed with a small quantity of the original flocculent precipitate. According to Berzelius, the precipitate obtained as above may contain carbonate of sodium. According to H. Rose, the precipitate formed by carbonate of sodium with sulphate of magnesium always contains $5Mg^2O$ to $4CO^2$, whatever may be the temperature and strength of the solutions.

The pharmaceutical preparation known as *Magnesia alba*, is a mixture of the several hydrocarbonates of magnesium, the proportions depending on the relative quantity of the precipitant, the degree of dilution, and the temperature at which precipitation takes place. It is prepared on the large scale by precipitating sulphate, nitrate, or chloride of magnesium with carbonate of potassium or sodium. Various mineral waters containing sulphate of magnesium, such as the Epsom water, are used for the purpose, also the mother-liquor of sea-water, of many salt-springs, and of many kinds of saltpetre; most of these liquids, however, contain lime, which must be previously separated by sulphate of potassium or sodium. After being well washed with hot water, it forms a very light, and bulky powder. The utmost degree of lightness is obtained by allowing the precipitate to freeze while still moist. (Gm. iii. 228.)

Acid Carbonate.—Magnesia alba shaken up with aqueous carbonic acid, forms a solution having a bitter taste and alkaline reaction, and containing, according to Soubeiran, just twice as much carbonic acid with the same quantity of magnesia as the normal salt (probably $MgHCO^3$). It becomes turbid at 75° C., but recovers its clearness on cooling. When heated to 50° C., or evaporated in vacuo, it deposits the trihydrated metacarbonate, $Mg^2CO^3 + 3aq.$ (Berzelius, Fritzsche.)

Carbonate of Magnesium and Ammonium, $Mg(NH^4)CO^3 + 2H^2O$, crystallises in translucent rhombohedrons from a mixture of the cold aqueous solutions of sulphate or chloride of magnesium and sesquicarbonate of ammonia, the latter in excess, or from a solution of hydrate of magnesium in sesquicarbonate of ammonia.

Carbonate of Magnesium and Potassium, $(Mg^4K^2H^2)C^4O^{12} + 8aq.$, is deposited after a few days in large crystals from a cold aqueous mixture of chloride or nitrate of magnesium with excess of diacid carbonate of potassium. The crystals become opaque and lose water at 100° C., and are decomposed by water, which dissolves the acid carbonates of potassium and magnesium, and leaves a residue consisting of the hydrocarbonate $3Mg^2CO^3.MgHO + 8aq.$ (Berzelius.)

H. Deville (Ann. Ch. Phys. xxxiii. 75), obtained the salt by the same process in microscopic crystals, apparently having the form of oblique rhombic prisms. By using sesquicarbonate of potassium instead of the diacid carbonate, he obtained, together with the preceding, another double salt, containing $MgHCO^3 + 2aq.$ The latter is obtained separately in small rhombic prisms by digesting *magnesia alba* for twelve or fifteen hours at 60° or 70° C., with diacid carbonate of potassium.

Carbonate of Magnesium and Sodium, $MgNaCO^3$, is obtained in anhydrous microscopic crystals by digesting *magnesia alba* in like manner with diacid carbonate of sodium. A mixture of a magnesium-salt with diacid carbonate of sodium yields no double salt, but only $Mg^2CO^3 + 3aq.$

CARBONATE OF MANGANESE.—The anhydrous carbonate occurs native as *Di-*

allogite, also called *Red Manganese, Rhodochrosite, Brown Spar, Manganspath.* It forms rhombohedral crystals, isomorphous with calcite, in which the principal is to the secondary axes as 0·8117 : 1, and the inclination of the faces meeting in the terminal edges = 106° 51′. The crystals are tabular, exhibiting the faces $R\,.\,-\frac{1}{2}R\ \infty R\,.\,0R$. It occurs also in globular and botryoïdal forms; likewise granular massive; occasionally as an impalpable powder. Specific gravity 3·4 to 3·6; of a variety from Kapnik, 3·592. Hardness 3·5 to 4·5. It is translucent, of rose-red or brownish colour, and vitreous lustre inclining to pearly. Streak white. Fracture uneven. Brittle. It is found in the Saxon mines, at Nagjày and Kapnik, in Transylvania, near Elbingerode in the Harz, &c. At Glendree in the county of Clare, Ireland, it forms a layer of yellowish-grey colour, two inches thick, below a bog. It also occurs in the pulverulent form, coating triplite, at Washington, Connecticut. It is generally mixed with the carbonates of calcium and magnesium, the proportion of carbonate of manganese varying from 97 to 75 per cent. A sample from Ireland, analysed by Gruner (Ann. Min. [3] xviii. 61), gave 97·1 per cent. Mn^2CO^3, 0·7 Fe^2CO^3, 1·0 Ca^2CO^3, 0·8 Mg^2CO^3, and 0·1 Mn^4O^3.

Anhydrous carbonate of manganese may be obtained artificially as a very fine amorphous, faintly rose-coloured powder, by heating chloride of manganese in a sealed tube with carbonate of sodium to 160° C., or with carbonate of calcium to 140°—170° from 12 to 48 hours. (Sénarmont, Compt. rend. xxviii. 693.)

By precipitating manganous salts with carbonate of potassium or sodium, a white precipitate is formed, which, after washing with boiling water, and drying in vacuo over oil of vitriol, is a snow-white tasteless powder, containing, according to the analyses of Ure, Turner, John, and Forchhammer, $2Mn^2CO^3 + aq.$ (Gm. iv. 214). According to H. Rose (Ann. Ch. Pharm. lxxx. 235) equivalent quantities of chloride of manganese and carbonate of sodium yield a precipitate containing $5Mn^2CO^3.2MnHO$.

Carbonate of manganese, whether anhydrous or hydrated, is permanent at ordinary temperatures, but when heated to redness in the air, assumes a dark brown colour, and is converted into manganoso-manganic oxide. Ignited in an atmosphere of hydrogen, it yields greenish-grey manganous oxide. Ignited in chlorine gas, it yields, according to Wöhler, a crystalline mixture of chloride of manganese and manganoso-manganic oxide:

$$4Mn^2CO^3 + Cl^2 = 2MnCl + 2Mn^2O^2 + 4CO^2.$$

Chlorine-water or aqueous hypochlorite of calcium converts it, first into manganoso-manganic oxide, afterwards into peroxide. When recently precipitated, it dissolves in ammoniacal salts. It is soluble in 7680 pts. of pure water, and in 3480 pts. of aqueous carbonic acid. (John.)

Carbonates of Mercury.—*Mercuric* nitrate gives with neutral or acid carbonate of potassium or sodium, a brown-red precipitate, containing $4Hg^2O.CO^2$, or $3Hg^2O.Hg^2CO^3$ (Setterberg, Pogg. Ann. xix. 60.) From mercuric chloride, alkaline bicarbonates precipitate, not a carbonate but an oxychloride.

Mercurous nitrate yields with carbonate of potassium, a black or yellow powder, consisting of *mercurous carbonate*, Hhg^2CO^3. It is very apt to give off carbonic acid; and the best way of obtaining it of definite composition is to mix mercurous nitrate with a slight excess of alkaline bicarbonate, set the mixture aside for a few days, and stir it frequently, then wash as quickly as possible, and dry in vacuo over oil of vitriol (Setterberg, *loc. cit.*) It is converted into mercuric oxide by exposure to the air. Alkalis blacken it, separating metallic mercury. (Gm. vi. 15.)

Carbonate of Methyl. See Carbonic Ethers.

Carbonate of Nickel.—The anhydrous salt, Ni^2CO^3, is obtained by heating chloride of nickel with alkaline carbonates in sealed tubes, in the same manner as carbonate of cobalt (p. 782), is a greenish-white crystalline powder, composed of minute rhombohedrons, scarcely attacked by strong acids at ordinary temperatures. (Sénarmont.)

A *hydrocarbonate of nickel*, $Ni^2CO^3.4NiH^3O^2$, called *Emerald-nickel*, occurs in the form of a stalactitic crust on chrome-iron ore, at Texas, Lancaster County, Pennsylvania, also at Swinaness in Unst, Shetland. It is amorphous, with an uneven somewhat scaly fracture. Specific gravity = 2·67 to 2·623. Hardness 3 to 3·25. Colour, emerald-green with strong vitreous lustre. Streak green. It gives off water when heated, and turns blackish. (B. Silliman, Jun. Sill. Am. J. [2] vi. 248.)

Hydro-nickelmagnesite, a mineral allied to the preceding, but containing magnesium as well as nickel, is found in the same localities in serpentine. (Shepard *ibid.* 250.)

Nickel-salts treated with alkaline carbonates, yield a pale apple-green, flocculent precipitate, which, after washing and drying, sometimes forms a loose, earthy, pale-green mass having a faint metallic lustre, sometimes, especially after continued washing with boiling water, a thick blackish-green mass, having a conchoïdal wavy fracture. The precipitates thus formed always contain water, their composition varying according to the temperature, strength, and proportions of the solutions employed. According to H. Rose (Ann. Ch. Pharm. lxxx. 237), the precipitate formed in the cold with sulphate of nickel and neutral carbonate of sodium consists, when dried at 100° C., chiefly of $Ni^2CO^3.3NiHO + 2aq.$; if boiled with a large quantity of water, it appears to take up water and lose carbonic acid. If heated in the air above 100°, it gradually gives off carbonic acid and water, and is partly converted into peroxide of nickel. Precipitated carbonate of nickel does not appear to be altered by digestion with bicarbonate of soda, even at 60° to 70°. (H. Deville.)

Carbonates of Nickel and Potassium.—By methods similar to those adopted with the corresponding cobalt-salts (p. 782), Deville obtained the salt $(NiK)CO^3 + 2aq.$ in shining apple-green microscopic needles, and $(Ni^2KH)C^2O^6 + 4aq.$, in light green crystals, apparently having the form of oblique rhombic prisms. The last was also obtained by Rose.

Carbonate of Nickel and Sodium, $(NiNa)CO^3 + 5aq.$, is obtained like the cobalt-salt, in small crystals, which appear to be cube-like rhombohedrons. (Deville.)

Carbonates of Palladium.—On adding an alkaline carbonate to a solution of palladium, a light yellow precipitate is formed, at first without evolution of carbonic anhydride; but on continuing the precipitation, effervescence ensues, and the precipitate turns brown. It retains a small quantity of carbonic acid when dry. (Berzelius.)

Carbonates of Potassium.—Three of these salts are known, all having the constitution of metacarbonates, viz. the *dipotassic* or *neutral carbonate*, K^2CO^3 or $K^2O.CO^2$, the *monopotassic* or *di-acid carbonate*, commonly called *bicarbonate*, $KHCO^3$ or $K^2O.H^2O.2CO^2$, and the *tetrapotassic* or *sesqui-acid carbonate*, $K^4H^2C^3O^9$, or $2K^2O.3CO^2 + H^2O$. The last has not been obtained in very definite form, and is perhaps only a mixture of the other two.

Dipotassic Carbonate, or *Neutral Carbonate of Potassium.* K^2CO^3. *Subcarbonate of Potash. Mild* or *Aërated Vegetable Alkali. Salt of Tartar. Purified Potash. Pearlash. Alkali vegetabile fixum. Cineres clavellati depurati.*—This salt is obtained chiefly from the ashes of plants. Living plants contain the potassium-salts of several vegetable acids, acetic, malic, tartaric, oxalic, &c.; and these salts, when calcined, are transformed into carbonate, which remains in the calcined residue mixed with charcoal and the various mineral salts contained in the plant, viz. sulphate, chloride, and silicate of potassium and sodium, besides carbonate of calcium and other insoluble matters. On treating the ash with water, the carbonate of potassium is dissolved, together with the alkaline sulphates and chlorides, and a residue is left, consisting of carbonate and phosphate of calcium, silica, clay, &c. The solution is evaporated to dryness, and the residue is sold as crude potash. Sometimes lime is stirred in with the solution during the evaporation, and then the carbonate of potassium is partly converted into hydrate or caustic potash. The quantity of potash obtained from different plants varies according to their nature, the most succulent yielding the largest amount, inasmuch as the alkaline salts are chiefly contained in the sap: hence herbaceous plants yield more than shrubs or trees. The different parts of the same plant also yield different quantities—the leaves more than the branches, the bark more than the wood.

The ashes of plants are used in all countries for the alkali which they contain, both as manure for the soil, and to yield a lye for the bleaching of linen; but it is only in countries where wood is very abundant, that potash can be advantageously prepared as a commercial product. Nearly all the potash used in the arts comes from America or from Russia.

Crude potash contains from 60 to 80 per cent. of carbonate of potassium, the remainder consisting of sulphate, chloride, and small quantities of silicate of potasssium together with organic matter which has not been completely burnt. This carbonate being much more soluble than the other potassium-salts, may, for the most part, be separated from them by digesting the crude potash for several days with its own weight of cold water, then decanting the liquid, quickly evaporating it, removing it from the fire as soon as it begins to show turbidity from the formation of small crystals, and leaving it to cool, stirring all the while to prevent the formation of large crystals, which would enclose mother-liquor in their cavities. The mother-liquor is then filtered off, the crystals washed with a small quantity of solution of pure carbonate of potassium, then dried and heated to incipient redness in vessels of cast-iron, silver, or platinum. The product thus obtained, called pearlash, contains only 2 or 3 per cent. of foreign matter, which, however, is difficult to remove.

Pure carbonate of potassium may be obtained by igniting acid tartrate of potassium (cream of tartar) in a crucible. A black residue is thereby obtained, consisting of carbonate of potassium and charcoal, which is often used as a reducing agent, under the name of *black flux*. The carbonate of potassium is separated from the charcoal by solution in water, filtration, and evaporation. If the solution has a brown colour from undecomposed organic matter, the salt must be again ignited.

Carbonate of potassium is sometimes prepared by throwing into a red-hot iron vessel, by small portions at a time, a mixture of 1 pt. cream of tartar and 2 pts. nitre. The carbon of the cream of tartar is then all burnt away by the oxygen of the nitre, and there remains a white mass called *white flux*, consisting almost wholly of carbonate of potassium. It frequently, however, contains small quantities of nitrite,—which may be avoided by diminishing the proportion of nitre used,—and always a little cyanide of potassium.

Pure carbonate of potassium is, however, more easily obtained from the acid carbonate or oxalate (binoxalate). The acid carbonate, $KHCO^3$, is found in commerce in large crystals very nearly pure. It may be further purified by recrystallisation, and, when ignited in a platinum or silver crucible, yields the pure neutral carbonate. The acid oxalate of potassium may be prepared by mixing hydrate of potassium with excess of oxalic acid, and purified by several crystallisations. When ignited, it leaves pure carbonate of potassium unmixed with charcoal. (Regnault.)

The impurities which may occur in commercial carbonate of potassium are the following: *Sulphate of potassium:* detected by the turbidity produced on adding chloride of barium to the solution acidulated with hydrochloric acid and diluted. *Chloride of potassium:* cloud produced by nitrate of silver in the solution acidulated by nitric acid. *Phosphate of potassium:* crystalline precipitate by sulphate of magnesium in solution treated first with hydrochloric acid, then with excess of ammonia. *Nitrate or nitrite of potassium:* reddish brown colour by ferrous sulphate in solution of the salt in excess of sulphuric acid. *Cyanide of potassium:* Prussian blue, formed by ferrosoferric sulphate and excess of hydrochloric acid. *Soda:* crystalline precipitate with acid metantimonate of potassium (p. 327). *Carbonate of calcium:* retained in solution, partly through the medium of the carbonate of potassium: cloud with oxalic acid after neutralisation with acetic acid. *Silica:* remains undissolved on acidulating with hydrochloric acid, evaporating to complete dryness, and digesting the residue in dilute hydrochloric acid. *Oxide of copper:* red-brown precipitate with ferrocyanide of potassium in acidulated solution.

Carbonate of potassium is very soluble in water, 1 pt. of the anhydrous salt dissolving, according to Osann, in 1·05 pt. of water at 3° C. (37·4° F.), in 0·9 pt. at 12·1° C. (54° F.), and in 0·49 pt. at 70° C. (158° F.) The most concentrated solution, containing 48·8 per cent. of the anhydrous salt, has a specific gravity of 1·54 at 15° C., and boils at 113° C. (235·4 F.) (Dalton). It has a strong alkaline taste and reaction, but is only slightly corrosive. A highly concentrated hot solution deposits on cooling rhombic octahedrons containing 20 per cent. of water, corresponding to the formula $K^2CO^3 + 2aq$.

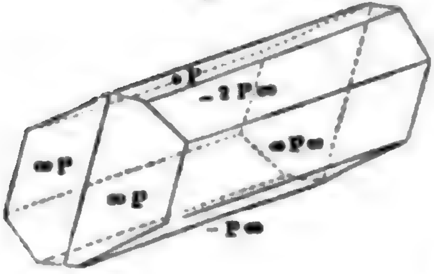
Both the crystals and the anhydrous salt deliquesce rapidly in the air, forming an oily liquid. The anhydrous salt melts at a red heat, volatilises at a white heat. It is not decomposed by any temperature in close vessels; but at a red heat, not sufficient to melt it, it is partly decomposed and converted into hydrate by a stream of aqueous vapour or moist air; it is not decomposed by dry air or dry hydrogen gas. Charcoal, at a bright red heat, decomposes it, with separation of potassium and formation of carbonic oxide and other products (see POTASSIUM). The aqueous solution, containing not less than 10 pts. of water to 1 pt. of the dry salt, is decomposed by lime at ordinary temperatures, and more quickly at the boiling heat, the carbonic acid being removed and caustic potassa produced. With more concentrated solutions, the reverse action takes place, caustic potassa abstracting carbonic acid from carbonate of calcium.

Carbonate of potassium is much used in chemical manufactures, especially for the preparation of soft soap, in glass making, and in the preparation of cyanide of potassium, ferrocyanide of potassium, Prussian blue, &c.; also for the preparation of nitrate of potassium from the nitrates of sodium, magnesium, and calcium.

Monopotassic Carbonate, or *Di-acid Carbonate of Potassium.* $KHCO^3 = K^2O.H^2O.2CO^2$. *Bicarbonate of Potassa. Berthollet's neutral Carbonate of Potassa.*—This salt is obtained by passing carbonic acid gas to saturation into a solution of 1 pt. of the commercial neutral carbonate in 4 or 5 pts. of water. Crystals of the acid carbonate soon form, and may be purified by washing with a small quantity of cold water. If a flocculent precipitate should form at first, consisting of alumina or silica, it must be removed by filtration. The carbonic acid evolved in alcoholic fermentation, or that which in some localities escapes from the soil, may be utilised for this purpose. A very good way of preparing the acid carbonate is to expose the mixture of neutral carbonate and charcoal, obtained by calcining cream of tartar and slightly moistened with water, to the action of carbonic acid gas; the presence of the charcoal greatly facilitates the absorption of the carbonic acid. The acid carbonate is dissolved out from the charcoal by boiling water and left to crystallise (Wöhler, Ann. Ch. Pharm. xxiv. 49). It must not be boiled in iron vessels, as it would dissolve a small quantity of the iron.

Acid carbonate of potassium crystallises in large rhomboïdal prisms belonging to the monoclinic system. Ratio of orthodiagonal to clinodiagonal to principal axis = 0·3734 : 1 : 0·491. Inclination of clinodiagonal to principal axis = 76° 35′. The crystals often exhibit the faces $\infty P . 0P . \infty P \infty . -P \infty . +2P \infty$ (*fig.* 125), the face $-P\infty$ frequently predominating so far as to obliterate the adjacent faces. $\infty P : \infty P = 138°$. Cleavage parallel to $\infty P \infty$, $-P\infty$, and $0P$. The crystals contain no water of crystallisation. When heated to 100° C., they give off water and carbonic anhydride, and are reduced to neutral carbonate: $2KHCO^3 - H^2O - CO^2 = K^2CO^3$.

Fig. 125.



Acid carbonate of potassium is much less soluble in water than the neutral carbonate. 100 pts. of water dissolve of it, according to Poggiale:

At 0° C. . . .	19·61 pts.	At 50° C. . . .	37·92 pts.
„ 10 . . .	23·33 „	60 . . .	41·35 „
„ 20 . . .	26·91 „	70 . . .	45·24 „

The aqueous solution when boiled gives off carbonic acid, and is gradually changed into neutral carbonate. The decomposition is sufficiently slow to admit of the purification of the acid carbonate from a boiling solution without much loss.

It dissolves but sparingly in boiling alcohol, only indeed to the amount of 1 pt. in 1200.

The aqueous solution of acid carbonate of potassium, mixed with the salts of other metals, generally forms double carbonates (pp. 782—788). It does not precipitate magnesium-salts in the cold, a character by which it is readily distinguished from the neutral carbonate.

Acid carbonate of potassium is much used in chemical operations where a pure potassium-salt is required, as it is very easily obtained in a pure and definite state. It is also used in medicine, in cases of gout and uric acid gravel.

Sesquicarbonate of Potassium?—A salt intermediate in composition between the two preceding, was said by Berthollet to be obtained in crystals, by mixing 100 pts. of the neutral with 131 pts. of the acid carbonate (1 at. K^2CO^3 with 2 at. $KHCO^3$), or by heating a solution of the di-acid carbonate as long as carbonic acid goes off; but according to H. Rose (Pogg. Ann. xxxiv. 149), the latter process yields almost pure neutral carbonate of potassium. The salt prepared by the first process should contain $K^4H^2C^3O^9$, or $2K^2O.3CO^2 + H^2O$; but its existence does not appear to have been satisfactorily proved.

Carbonate of Silver, Ag^2CO^3, is produced by precipitating nitrate of silver with an alkaline carbonate. It is white at first, but becomes yellow when the soluble salts are washed out, and blackens when exposed to light or gently heated. It dissolves readily in strong ammonia, and the solution treated with absolute alcohol yields a precipitate containing ammonia and carbonate of silver. (Berzelius.)

At 200° C. it gives off carbonic anhydride, and leaves pure oxide of silver, which begins to give off oxygen at 250°. By precipitating nitrate of silver with a large excess of alkaline carbonate and boiling, a basic carbonate is obtained, having, when dried at 100°, the composition $3Ag^2O.CO^2$, or $Ag^2CO^3.2Ag^2O$, perhaps only a mixture. (H. Rose, Ann. Ch. Pharm. lxxxiv. 202.)

Carbonates of Sodium.—Three of these salts are known, corresponding in composition to the potassium salts.

Disodic Carbonate, or *Neutral Carbonate of Sodium*, Na^2CO^3. *Subcarbonate of Soda. Soda. Mild mineral alkali. Alkali minerale fixum.*—This salt exists in the soda-lakes of Egypt and Hungary, and in the volcanic springs of Iceland, &c.; it also frequently occurs, mixed with sulphate of sodium, in the form of an efflorescence on walls, being formed from sodium-salts contained in the mortar. It is largely used in the arts, and was formerly obtained from *barilla*, the ash of *Salsola soda* and other plants growing on the sea-shore, and from the ash of sea-weed called *kelp*: but at the present day, nearly all the soda of commerce is obtained from common salt, by a process invented by Leblanc, towards the end of the last century, and perfected by D'Anfret and D'Arcye. This process consists of three stages:

1. The conversion of chloride of sodium into sulphate by heating it with sulphuric acid.
2. The conversion of the sulphate into carbonate by heating it in a reverberatory

furnace with chalk or limestone and coal. The materials are mixed in the proportion of about 3 pts. of dry sulphate of sodium, 3½ pts. chalk, and 2 pts. coal. The sulphate of sodium is reduced to sulphide, with evolution of carbonic oxide; and the sulphide of sodium is converted by the carbonate of calcium into carbonate of sodium and sulphide of calcium, which, by taking up lime, is for the most part converted into an insoluble oxysulphide of calcium:

$$2Na^2SO^4 + 3Ca^2CO^3 + C^9 = 2Na^2CO^3 + Ca^6S^2O + 10CO.$$

Part of the carbonic acid is, however, driven off from the lime by the heat, before it can act on the sulphide of sodium, and consequently, the fused mass contains, besides carbonate of sodium, a variable but always large amount of caustic soda.

The crude soda obtained by this process, has the appearance of dark-grey, half-vitrified balls,—hence called "black balls,"—being brought into this form by stirring while in the semi-fused state. It varies considerably in composition, as the following analyses will show, one of a sample from Cassel analysed by Unger, another from Newcastle, by Richardson.

Composition of Black Balls, or Crude Soda.

	Cassel.	Newcastle.
Carbonate of sodium	23·57	9·89
Caustic soda	11·12	25·64
Sulphate of sodium	1·99	3·64
Chloride of sodium	2·54	0·60
Carbonate of calcium	12·90	15·67
Oxysulphide of calcium	34·76	35·57
Sulphide of iron	2·45	1·22
Silicate of magnesium	4·74	0·88
Charcoal	1·59	4·28
Sand	2·02	0·44
Water	2·10	2·17
	99·78	100·00

3. *Purification.*—The crude or ball soda, after being crushed under millstones and sifted, or loosened and disintegrated by hot vapour, is lixiviated with warm water, which dissolves up the carbonate of sodium and the other soluble salts, leaving the oxysulphide of calcium undissolved. To effect the extraction with the smallest possible quantity of water, the crude soda is placed in perforated sheet-iron boxes, suspended just below the surface of the liquid, and is subjected to a continuous process of exhaustion in a series of lixiviating tanks, arranged somewhat like the pans for the evaporation of boric acid (p. 637). Each box containing the crude soda is first suspended in the lowest cistern, which contains a nearly saturated lye, then transferred to the next, which contains a somewhat weaker lye, and so on till it arrives at the highest, into which pure water is admitted from a cistern. When the lye in the lowest tank is saturated, it is transferred to the evaporating pan, its place being supplied by that in the next, which in its turn is replaced by the third, &c. In this manner, each portion of liquid gets thoroughly saturated, and the ball soda completely exhausted of soluble salts. The concentrated solution is boiled down to dryness, and yields a salt consisting chiefly of carbonate of sodium mixed with caustic soda and sulphide. This is called *soda-salt.*

4. To purify this product further, it is mixed with one-fourth of its bulk of sawdust, and exposed to a low red heat in a reverberatory furnace, for about four hours: the carbonic acid produced by the combustion of the sawdust, then converts the caustic soda into carbonate; also the sulphide, with evolution of sulphuretted hydrogen. This product contains about 50 per cent. of alkali, and forms soda-salt of the best quality.

5. To obtain *crystallised carbonate*, the purified soda-salt is dissolved in water, and the liquid when clarified is boiled down till a pellicle forms on the surface. The solution is then run into shallow crystallising vessels, and after standing for a week, the mother-liquor is drawn off, and the crystals are drained and broken up for the market. The crystals thus obtained contain 10 at. of water. The mother-liquor, which contains the foreign salts is evaporated to dryness for soda-salt.

The crystallisation of carbonate of sodium generally affords a safe guarantee of its purity; the crystals also dissolve in water much more quickly than the anhydrous salt, and are therefore more convenient for many purposes. But when the salt is required in the anhydrous state, as for glass-making, or as a flux in metallurgic operations, or where large quantities are wanted, as in the soap-manufacture, the soda-salt is preferred, as the large quantity of water in the crystals (nearly 63 per cent.) greatly increases the cost of transport. For some purposes, the crude soda as it leaves the furnace is sufficiently pure. In preparing it to be sold for such purposes, sulphate of sodium is used containing 10 to 12 per cent. of common salt; this remains unchanged in the soda, and communicates to it the property of easily falling to pieces in damp air, thus obviating the necessity of grinding.

For further details respecting the soda-manufacture, see *Miller's Chemistry*, vol. ii.; *Ure's Dictionary of Arts, Manufactures, and Mines*, iii. 720; *Chemical Technology, by Richardson* and *Watts;* Payen, *Précis de Chimie industrielle*, 4^{me} éd. i. 296.

Other methods of obtaining carbonate of sodium from the chloride have been proposed, but none of them appear to be able to compete with that above described.—1. Sulphate of iron produced by the oxidation of iron pyrites, is a cheap article, and has been proposed as a substitute for sulphuric acid in the first stage of the process: sulphate of sodium and chloride of iron are formed, the latter volatilising; or the two salts are dissolved together in water, and the solution is exposed to a low temperature, whereupon sulphate of sodium crystallises out, while chloride of iron remains in solution; or the sulphate of sodium may be made to crystallise out by raising the liquor to the boiling point.—2. Sulphate of sodium may be formed by roasting iron pyrites in a reverberatory furnace with common salt.—3. Sulphate of sodium is decomposed by a solution of caustic baryta or strontia, these earths being procured by decomposing the native sulphates with steam at a red heat; the sulphuric acid thereby set free might be used for converting the chloride of sodium into sulphate (Tilghmann).—4. Chloride of sodium is decomposed by hot steam in presence of alumina, whereby aluminate of sodium is formed; and the solution of this salt is decomposed by a current of carbonic acid gas (Tilghmann).—5. Ammonia gas is passed into a solution of chloride of sodium; then carbonic acid, whereby chloride of ammonium and acid carbonate of sodium are produced:

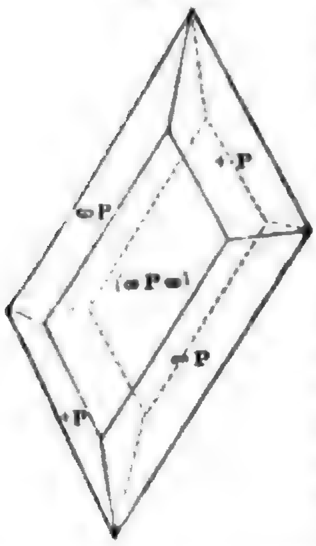
$$NaCl + NH^3 + CO^2 + H^2O = NaHCO^3 + NH^4Cl.$$

The acid carbonate of sodium being the less soluble salt of the two, crystallises out; it is converted into neutral carbonate by heat, and the carbonic acid evolved is used again. The mother-liquor containing the sal-ammoniac is boiled, to drive off any carbonate of ammonium that it may contain, and this salt is collected; the solution is then boiled with lime, to liberate the rest of the ammonia. In this manner the operation may be conducted with but little loss. (Schloessing and Roland.)

The impurities found in commercial carbonate of sodium are, *sulphide*, *hyposulphite*, *sulphate*, *chloride* and *ferrocyanide of sodium;* also *potassium-salts*, *carbonate of calcium*, and *carbonate of magnesium*. It may be purified by repeated crystallisation, or by washing the commercial crystals with cold water, dissolving them in hot water, stirring and cooling rapidly, to prevent formation of large crystals, then draining off the mother-liquor, and washing the crystalline powder with cold water. (Gay-Lussac.)

Neutral carbonate of sodium in the anhydrous state, is a white powder composed of translucent particles. It has a specific gravity of 2·4659 (Karstin). It melts at a moderate red heat, more easily than carbonate of potassium. It is quite undecomposible by heat in close vessels, but is easily decomposed when heated to redness in a current of steam or moist air, less easily in a current of dry air or hydrogen (H. Rose). It is decomposed by charcoal at a bright red heat, yielding carbonic oxide and sodium. In contact with water, it becomes heated, and forms a hydrate which dissolves. It has an alkaline taste and reaction, but is even less caustic than carbonate of potassium.

Fig. 126.



Hydrates.—There are several *hydrates* of neutral carbonate of sodium. — *a.* The ordinary crystals which separate from a moderately strong solution at ordinary temperatures, contain 10 at. (62·69 per cent.) water, $Na^2CO^3 + 10H^2O$. They belong to the monoclinic system. Orthodiagonal: clinodiagonal: principal axis = 0·7049 : 1 : 1·0452. Inclination of clinodiagonal = 57·40°. Ordinary combination + P . ∞ P . [∞ P ∞] (*fig.* 126); ∞P : ∞ P = 100° 20′. Cleavage tolerably distinct parallel to ∞ P ∞, less distinct parallel to [∞ P ∞]. Specific gravity = 1·423 (Haidinger). They effloresce in moderately dry air, crumbling to a white powder, and giving off 5 at. water at 12·5° C. and 9 at. at 38° (Schindler); 9 at. also in vacuo over oil of vitriol (Blücher). The 10-hydrated salt occurs as a natural product called *natron*, together with the mono-hydrate, at the soda-lakes of Egypt and Hungary, at Vesuvius, Etna, and in various parts of Asia, Africa, and America. (Dana, ii. 455.)

a. $Na^2CO^3 + 15aq.$ is obtained in crystals, when a solution of the neutral salt is exposed to a temperature of − 20° C., and the frozen water is afterwards allowed to liquefy; and $Na^2CO^3 + 9aq.$ by repeatedly crystallising a solution which at first contains a portion of acid carbonate. (Jacquelain, Compt. rend. xxx. 106.)

b. $Na^2CO^3 + 8\ aq.$ crystallises in right rhombic prisms with four-sided summits, when the 10-hydrated salt is melted and left to cool, or from a hot-saturated aqueous solution, apparently at a temperature lower than the crystallising point of the mono-hydrated, and higher than that of the deca-hydrated salt. (Thomson, *Annals of Philosophy*, 26, 44.)

c. $Na^2CO^3 + 7aq.$—This hydrate crystallises in two forms, (*a*) rhombohedral; (*b*) in trimetric crystals of the same form as Thomson's salt (which, according to Loewel, contains, not 8 at. but 7 at. water). When a solution saturated at the boiling heat is enclosed in a flask, which is corked immediately after the boiling has ceased, no crystals are deposited from it for a long time on cooling down to between 25° and 18° C.; but on cooling below 8° it deposits chiefly the trimetric 7-hydrated salt. Between 16° and 10°, it yields the rhombohedral salt (*a*), which redissolves between 21° and 22°, forms again at 19°, and on cooling from 10° to 4° becomes opaque, and passes into *b.* After cooling to a lower temperature and for a longer time, when the state of supersaturation ceases, the whole is converted into a mass of crystals of the deca-hydrated salt. (H. Loewel, Ann. Ch. Phys. [3] xxxiii. 334.)

d. $Na^2CO^3 + 6aq.$ crystallises from a solution of protosulphide of sodium exposed to the air, and frequently also from a mixed solution of carbonate of potassium and chloride of sodium. (Mitscherlich, Pogg. Ann. viii. 441.)

e. $Na^2CO^3 + 5aq.$ is formed when the 10-hydrated salt effloresces at 12·5° C. (Schindler), also when the same salt is melted in its water of crystallisation, and after the mono-hydrated salt has crystallised out between 70° and 80° C., the remaining liquid is kept for some time at 34°; it is also formed from the mono-hydrated salt by exposure to the air (Berzelius). It was once accidentally obtained at the Buxweiler soda works, in transparent rhombic octahedrons, which effloresced slightly in the air, and when dissolved in water and evaporated at 30° C. yielded the same salt. (Persoz, Pogg. Ann. xxiii. 303.)

f. $Na^2CO^3 + aq.$ is formed from the deca-hydrate by efflorescence, and is found native as *thermonatrite*, in the same localities as natron, and is indeed the more common salt of the two. It forms rectangular tables of the trimetric system with bevelled edges.

The same hydrate separates from a solution of the neutral carbonate concentrated by evaporation at the boiling heat, a circumstance which is made available in the soda manufacture for the purification of the salt, the crystalline powder which separates from the boiling solution being taken out and drained; if left to cool in the solution, it would redissolve. It does not undergo the aqueous fusion when heated, but gives off its water and becomes opaque at 87° C. It absorbs water from moist air, and is converted into the pentahydrate. In a warm atmosphere, it absorbs carbonic acid and forms sesquicarbonate.

Solution of Carbonate of Sodium.—According to Poggiale, 100 pts. of water dissolve of the anhydrous salt, 7·08 pts. at 0° C., 16·66 at 10°, 25·93 at 20°, 30·83 at 25°, 35·90 at 30°, and 48·5 at 104·6°, which is the boiling point of the saturated solution. According to Anthon, the 10-hydrated salt dissolves in 2 pts. of cold, and much less than 1 pt. of hot water. According to Loewel (*loc. cit.*) 100 pts. of a saturated solution contain of the 10-hydrated salt, 7 pts. at 0° C., 12·1 pts. at 10°, 16·2 pts. at 15°, 21·7 pts. at 20°, 28·5 pts. at 25°, 37·2 pts. at 30°, 51·7 pts. at 38°, and 45·5 pts. at 104°. Hence it appears that there is a maximum solubility at 38° C.

Solutions of carbonate of sodium are capable of assuming the state of supersaturation, like those of the sulphate. A solution saturated at the boiling heat and immediately enclosed in a sealed tube or a well corked flask, remains supersaturated at common temperatures, and frequently even when cooled several degrees below 0° C. Keeping the air in contact with the liquid from agitation, as by covering the hot solution with a glass shade, is often sufficient to prevent crystallisation at ordinary temperatures; but access of air then causes immediate solidification, attended with rise of temperature. The supersaturated solutions, as already observed, deposit the 7-hydrated salt in two different modifications, according to temperature (*vid. sup.*)

Monosodic Carbonate. Di-acid Carbonate of Sodium. Bicarbonate of Soda. $NaHCO^3$ or $Na^2O.H^2O.2CO^2$.—This salt exists in solution in alkaline mineral waters. It is prepared: 1. By passing carbonic acid gas into a solution of the neutral carbonate as long as it is absorbed.—2. By exposing the effloresced neutral carbonate placed on trays in a wooden case to an atmosphere of carbonic acid.—3. By adding commercial carbonate of ammonia (which is chiefly bicarbonate) to an equal weight of chloride of sodium, dissolved in three times its weight of water, stirring the whole well together, and leaving it to stand for several hours. Monosodic carbonate then separates in crystalline grains, while chloride of ammonium remains in solution (p. 794)

$$NaCl + NH^4.H.CO^3 = NaHCO^3 + NH^4Cl.$$

The precipitate is separated from the liquid by pressure in a screw press, but it always retains a portion of chloride of sodium.

Monosodic carbonate crystallises in oblique four-sided tables, and is sometimes obtained by the first method in crystals of considerable size; the second and third methods yield it in the form of a crystalline powder. It has a slight alkaline taste and reaction, and is permanent in dry air at ordinary temperatures. At a red heat, it gives off water and carbonic acid, and is reduced to anhydrous neutral carbonate.

100 pts. of water dissolve of monosodic carbonate, 8·95 pts. at 0° C., 10·04 pts. at 10°, 11·15 pts. at 20°, 12·24 pts. at 30°, 14·45 pts. at 40°, and 16·69 pts. at 70° (Poggiale). The solution gives off carbonic acid slowly at ordinary temperatures, more quickly at 70° C., rapidly at the boiling heat, and is ultimately reduced to neutral carbonate. It does not precipitate magnesium-salts in the cold, but at the boiling heat carbonic acid escapes and a precipitate of carbonate of magnesium is formed; this character distinguishes it from the neutral carbonate. Acid carbonate of sodium is used for the preparation of effervescing powders, and as a remedy in certain calculous disorders.

Tetrasodic Carbonate or *Sesquicarbonate of Sodium.* $Na^4H^2C^3O^8 + 2aq. = 2Na^2O.H^2O.3CO^2 + 2aq.$ — This salt, which may be regarded as a compound of the mono- and di-sodic carbonates ($2NaHCO^3 + Na^2CO^3$), is found in Africa, in the province of Sakenna, two days' journey from Fezzan, where it is called *trona;* it occurs at the foot of a mountain, forming a crust, varying in thickness from an inch to that of the back of a knife; also as *urao* at the bottom of a lake in Maracaibo, South America; efflorescences of it occur also near the Sweetwater River, Rocky mountains, mixed with sulphate and chloride of sodium (Dana, ii. 454). It is produced artificially: 1. By mixing the mono- and di-sodic carbonates in the proportions above indicated, melting them together, drying, and exposing the dried mass to the air of a cellar for some weeks; it then absorbs water, becomes crystalline, and contains spaces filled with shining crystals of tetrasodic carbonate. From a hot solution of mono- and di-sodic carbonates, the two salts crystallise out separately on cooling (Hermann, J. pr. Chem. xxvi. 312).—2. A solution of the monosodic salt, concentrated by boiling, but not boiled long enough to reduce it to the disodic salt, deposits the tetrasodic salt on cooling.—3. If 4 oz. of alcohol be poured on the top of a solution containing 100 grains of the disodic and 152 grains of the crystallised monosodic carbonate in 4 oz. of water, fine clear needle-shaped crystals of the tetrasodic salt form, after some days, at the surface of separation of the two liquids, while at the bottom of the solution, large crystals of the disodic carbonate are found covered by a crust of the monosodic salt. (Winckler, *Gmelin's Handbook*, iii. 83.)

The crystals of the native salt belong to the monoclinic system. Orthodiagonal: clinodiagonal: principal axis = 0·3552 : 1 : 1·282. Inclination of clinodiagonal to principal axis = 53° 50′. Observed combination $\infty P . 0P . + P\infty$, prismatically elongated in the direction of the orthodiagonal. $\infty P : \infty P = 132° 30′$. Cleavage very perfect, parallel to $+ P\infty$. They are colourless, transparent, or translucent, with vitreous lustre. Specific gravity 2·112. Hardness 2·5 to 3. Structure foliated, radiating; fracture conchoïdal. The artificial crystals are small, and of the same form as the native crystals. The salt has an alkaline taste and reaction, and is not efflorescent. At a red heat, or when its aqueous solution is boiled for many hours, it is reduced to the neutral carbonate. It is intermediate in solubility between the two preceding salts. According to Poggiale, 100 pts. of water dissolve of it, 12·63 pts. at 0° C., 18·30 pts. at 20°; 38·95 pts. at 40°; 29·68 pts. at 60°; 35·80 pts. at 80°; and 41·59 pts. at 100°. The solution is not rendered turbid by 1 pt. of sulphate of magnesium dissolved in 10 pts. of water. Evaporated in vacuo over oil of vitriol, it yields a mass of crystals composed of the mono- and di-sodic carbonates together. (H. Rose, Pogg. Ann. xxxii. 160.)

Carbonate of Sodium and Potassium. $KNaCO^3 + 6aq.$—Separates from a solution containing equivalent quantities of the component salts, in monoclinic crystals exhibiting the faces $\infty P . \infty P\infty . [\infty P\infty] . \infty P2 . [\infty P2] . 0P . + P . + P2 . + P\infty . + 2P\infty [P\infty] . + 2P\infty$. Inclination of faces; $\infty P : \infty P$ in the clinodiagonal principal section = 108° 34′; $0P : \infty P\infty = 131° 48′$; $0P : \infty P = 122° 46′$; $0P : + P\infty = 124° 48′$; $0P : + 2P\infty = 84° 19′$ (Marignac, Compt. rend. xlv. 650). Nearly the same angular values were observed by Sénarmont. The crystals are permanent in the air. A salt containing $K^2Na^4C^3O^9 + 18aq.$ is mentioned by Margueritte (Ann. Ch. Pharm. lvi. 220) as crystallising from the mother-liquor of ferrocyanide of potassium, and from a concentrated solution of the simple salts; but Marignac was not able to obtain this compound, and is of opinion that the formula is deduced from an incorrect analysis.

A mixture of the neutral carbonates of sodium and potassium in equivalent proportions, fuses at a much lower temperature than either of the salts separately, doubtless in consequence of the formation of the double salt. Such a mixture is very useful in the fusion of silicates, &c.

Carbonate of Sodium and Calcium, $CaNaCO^3 + 5aq$.– Occurs abundantly, as Gay-Lussite, at Lagunilla near Merida, in Maracaibo, covering *urao;* found also at Sangerhausen in Thuringia. The crystals are monoclinic. Inclination of axes = 78° 27′; $\infty P : \infty P = 68° 50'$. Cleavage perfect parallel to ∞P: less perfect parallel to $0P$. They are yellowish-white, translucent, double refracting, extremely brittle, with conchoïdal fracture, and exhibit a vitreous lustre on the broken surface. Specific gravity = 1·92—1·99. Hardness = 2–3. The mineral decrepitates when heated, and becomes opaque from loss of water. In the hydrated state it dissolves sparingly in water, without decomposition; but the anhydrous salt is resolved by water into carbonate of sodium and carbonate of calcium. Crystals of Gay-Lussite, altered to calcite, are sometimes called *natrocalcite*. (Dana, ii. 453).

The salt may be prepared by fusing the anhydrous carbonates of sodium and calcium together in atomic proportions.

The double salts of carbonate of sodium with other metals, magnesium, cobalt, zinc, &c., are described with the carbonates of those metals.

CARBONATE OF STRONTIUM. Sr^2CO^3. — Occurs native as *Strontianite*, at Strontian in Argyleshire, where it was first observed; also in Yorkshire, at the Giant's Causeway, at Clausthal in the Harz, at Bräunsdorf in Saxony, Leogang in Saltzburg, and other localities. It forms crystals of the trimetric system, isomorphous with arragonite and witherite. Ratio of brachydiagonal to macrodiagonal to principal axis = 0·6026 : 1 : 0·7237. The crystals are often prismatic from predominance of the faces $\infty P \,.\, \infty\breve{P}\infty$ and $\breve{P}\infty$. Cleavage tolerably perfect parallel to ∞P, less perfect parallel to $2\breve{P}\infty$. Specific gravity 3·605—3·713. Hardness 3·5 to 4. Colour white with various shades of grey, green, yellow, and brown. Streak white. Lustre vitreous. Transparent or translucent. Fracture uneven. Brittle. Before the blowpipe it melts on the edges and swells up, emitting a brilliant light, and when strongly heated in the reducing flame, imparts to it a reddish tinge. Strontianite occurs altered to cœlestine by the action of soluble sulphates. *Baryto-strontianite*, from Stromness in Orkney, appears to be a mechanical mixture of the carbonates of strontium and barium.

Carbonate of strontium obtained by precipitation is a white substance, smooth to the touch and has but little cohesion. It dissolves in 18045 pts. of cold water, and in 56545 pts. of water containing ammonia or carbonate of ammonium (Fresenius); in 300,000 pts. of water, whether cold or hot (Bineau, Compt. rend. xli. 509); in 833 pts. of water saturated with carbonic acid at 10° C. (Lassaigne), and in this state it occurs in some mineral waters, whence it crystallises by evaporation in needle-shaped crystals. When heated in close vessels, it does not give off carbonic anhydride at any temperature short of that of a forge fire; but in a stream of aqueous vapour or moist air, the decomposition takes place at a lower temperature, with formation of hydrate of strontium. It is not decomposed by solutions of alkaline sulphates at any temperature. (H. Rose, Pogg. Ann. xcv. 284).

CARBONATE OF THORINUM.—Alkaline carbonates, added to solutions of thorinum-salts, throw down a basic salt, with evolution of carbonic acid. Moist hydrate of thorinum absorbs carbonic acid from the air. The anhydrous earth is not soluble in water containing carbonic acid. (Berzelius.)

CARBONATES OF URANIUM.—These salts do not appear to exist in the separate state. Alkaline carbonates throw down from uranous chloride a precipitate of uranous hydrate; from uranous sulphate, a basic sulphate; from uranic salts, precipitates consisting of double carbonates.

Ammonio-uranic Carbonate, $2[(NH^4)^2O.CO^2] + U^4O^3.CO^2$ or *Carbonate of Uranyl* * *and Ammonium*, $\left.\begin{matrix}(NH^4)^4\\(U^2O)^2\end{matrix}\right\}C^3O^9$.—On digesting the precipitate thrown down by ammonia or carbonate of ammonia from a uranic salt in a solution of carbonate of ammonia at 60°—80° C., till the liquid is saturated, then filtering hot, and leaving the filtrate to cool, this salt separates in small transparent yellow crystals. It decomposes slowly in the air at common temperatures, more quickly when heated, ultimately leaving a residue of brick-red uranic oxide. It dissolves in 20 pts. water at 15° C., more easily in water containing carbonate of ammonia. The solution, when boiled, gives off carbonate of ammonia, and deposits the whole of the uranium as a yellow precipitate, consisting, according to Arfvedson, of uranic oxide with small quantities of ammonia and carbonic acid; according to Péligot, of uranate of ammonium; according to Ebelmen, of uranic hydrate containing 2 per cent. ammonia, but no carbonic acid. (Ebelmen, Ann. Ch. Phys. [3] v. 189; Delffs, Pogg. Ann. lv. 229.)

Potassio-uranic Carbonate, $K^4(U^2O)^2C^3O^9$.—Obtained by dissolving in acid carbonate of potassium the precipitate thrown down from uranic salts by the neutral carbonate,

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* Uranyl, U^2O, is a monatomic radicle which may be supposed to exist in the uranic salts, *e.g.* uranic nitrate, $U^4O^3.N^2O^5 = (U^2O)NO^3$. (See URANIUM.)

evaporating at a gentle heat, and recrystallising. It forms a bright-yellow crystalline crust, which gives off carbonic anhydride at 300° C., and when heated to redness leaves a red-brick mixture of uranate and carbonate of potassium. It dissolves in 13·5 pts. of water at 15° C. without decomposition, but is partially decomposed by boiling water. which throws down uranate of potassium. The same compound is deposited after a while from a cold solution of the double carbonate, if very dilute and not containing excess of carbonate of potassium. Caustic potash precipitates the whole of the uranium as uranate of potassium, even in the presence of a large excess of carbonate of potassium. Acids, if not added in large excess, produce the same light yellow precipitate as is produced by carbonate of potassium in uranic salts. The double salt is insoluble in alcohol. (Ebelmen, *loc. cit.*)

Sodio-uranic Carbonate, $Na^4(U^2O)^2C^3O^9$.—Prepared like the preceding, which it resembles.

Calcio-uranic Carbonate, $Ca(U^2O)CO^3 + 10aq.$ — Found native as *Liebigite*, in amorphous rounded masses, having a distinct cleavage in one direction, transparent, of a beautiful apple-green colour, and vitreous lustre on the fractured surface. Hardness 2 to 2·5. Gives off water when gently heated and turns blackish-grey; does not fuse at a red heat, but turns black, and acquires an orange-red colour on cooling. Occurs, with Medjidite, near Adrianople, also at Johanngeorgenstadt, and in the Joachimsthal. (J. L. Smith, Ann. Ch. Pharm. lxvi. 253.)

A *calcio-uranous carbonate*, $CaUCO^3 + \frac{2}{3}$ aq., occurring in siskin-green scaly aggregations on pitch-blende at the Elias mine near Joachimsthal, has been examined by Vogl and Lindacker (Jahrb. k. k. geol. Reichsantalt, iv. 1853, 221). A carbonate of uranium, copper, and calcium, called *Voglite*, which may be regarded as an orthocarbonate $(U^4Cu^6Ca^2H^8)C^5O^{20} + 10aq.$, occurring in the same locality in aggregations of green dichroic, crystalline, pearly scales, has also been examined by Lindacker (*loc. cit.*)

CARBONATE OF YTTRIUM, Y^2CO^3 (containing also erbium and terbium).—Precipitated from yttrium-salts by carbonate of sodium, with 13 at. water in the cold, with 2 at. at the boiling heat. It is not easily decomposed by heat; dissolves sparingly in water containing carbonic acid; decomposes ammoniacal salts and dissolves in the liquid. Its solution in carbonate of ammonia deposits, after a time, if concentrated, a white crystalline double salt, which does not redissolve in carbonate of ammonia. Carbonate of yttrium dissolves also, though less easily, in the carbonates of potassium and sodium. (Berzelius.)

CARBONATES OF ZINC.—The *neutral carbonate*, or *metacarbonate*, Zn^2CO^3, occurs native as calamine (p. 713). It is doubtful whether this anhydrous salt can be obtained by precipitation. According to Schindler (Gmelin's Handbook, v. 16) it is produced by precipitating a solution of 1 at. sulphate of zinc in 10 pts. water with 1 at. diacid carbonate of potassium or sodium; but, according to Berzelius, the precipitate thus formed is $Zn^2CO^3.3ZnHO$.

Hydrocarbonates. *Zinc-bloom*, which occurs in nature as an earthy incrustation and in reniform masses, has, according to Berzelius, the composition $5Zn^2O.CO^2 + 3aq.$, or $Zn^2CO^3.Zn^2O.6ZnHO$; according to the analyses of Smithson and Bonsdorff, it is $3Zn^2O.CO^2 + 3aq.$, or $Zn^2CO^3.4ZnHO + aq.$ It is dull and opaque, with white, greyish, or yellowish colour, and makes a shining streak. Specific gravity = 3·58 to 3·6. Hardness = 2 to 2·5 (Gm. vi. 15). *Aurichalcite*, or *green calamine* (p. 476), found in the Altai, and at Matlock in Derbyshire, may be regarded as $Zn^2CO^3.3ZnHO$, in which the zinc is partly replaced by copper. *Buratite* (p. 686) is a hydrocarbonate of zinc containing copper and calcium, perhaps a mixture.

The precipitates formed by alkaline carbonates in solutions of zinc-salts, all appear to contain water, their constitution varying with the strength and temperature of the solutions, and with the nature and proportion of the precipitant. The results obtained in individual cases are variously stated by different authors; those obtained by H. Rose (Pogg. Ann. lxxxv. 107; Ann. Ch. Pharm. lxxxiv. 210) are as follows:

a. With 1 *at. Sulphate of Zinc and* 1 *at. Neutral Carbonate of Sodium.*—When the solutions are cold and concentrated, the precipitate consists mainly of $Zn^2CO^3.3ZnHO$ $\frac{2}{3}$aq., it remains unaltered at 60° C., but, after drying at 100°, is composed of $2Zn^2CO^3.7ZnHO + \frac{1}{2}aq.$ Very dilute cold solutions and concentrated boiling solutions yield a precipitate consisting mainly of $Zn^2CO^3.ZnHO$, or Zn^3HCO^4, combined with variable quantities of water.

b. With excess of Neutral Carbonate of Sodium.—The precipitate from cold solutions contained, when dried at 100° C., $5Zn^2CO^3.18ZnHO$; from moderately warm solutions $3Zn^2CO^3.10ZnHO$ (at 100°), but if very large quantities of liquid were used, it consisted of $Zn^2CO^3.2ZnHO$.

c. With 1 *at. Sulphate of Zinc and* 1 *at. Acid Carbonate of Sodium.* ($NaHCO^3$).—The precipitates contain more carbonic acid than the preceding. When they are dried in vacuo, a large quantity of carbonic acid escapes, and there remains the compound $Zn^2CO^3.3ZnHO + aq.$

d. With excess of Acid Carbonate of Sodium.—From cold solutions a precipitate was several times formed containing $2Zn^2CO^3.5ZnHO + \frac{1}{2}aq.$ (at 100°). A precipitation on the large scale, with rather warm solutions, yielded $Zn^2CO^3.ZnHO$. The precipitate obtained with cold solutions, after standing for some time, had, when air-dried, but not washed, the composition $3(2Zn^2CO^3.ZnHO. + \frac{5}{2}aq.$; after drying at 100°, it became $2Zn^2CO^3.ZnHO$.

e. With excess of Acid Carbonate of Potassium.—The precipitate not washed, but dried between filtering paper, had the composition $2Zn^2CO^3 + 2H^2O$. After washing with cold water and drying in the air, it became $4Zn^2CO^3 + 5aq.$; at 100° it was reduced to $4Zn^2CO^3 + aq.$; and at 200° to $5Zn^2CO^3 + aq.$

According to Schindler, basic salts having the composition $8Zn^2O.CO^2 + 2aq.$, or $Zn^2CO^3.7Zn^2O.2H^2O$ and $4Zn^2O.CO^2.2H^2O$, or $Zn^2CO^3.3Zn^2O.2H^2O$, are obtained by precipitating the corresponding sulphates of zinc with carbonate of sodium. According to Boussingault, ordinary sulphate of zinc precipitated with sesquicarbonate of sodium at ordinary temperatures, yields the salt $2Zn^2O.CO^2 + 2aq.$, or $Zn^4CO^4 + 2aq.$ According to Schindler, hot solutions of these salts yield a precipitate of the same composition as zinc-bloom. (Gm. v. 15.)

All the hydrocarbonates of zinc give off their water and carbonic anhydride at 200° C., and are reduced to zinc-oxide, Zn^2O. The native carbonate remains unaltered at 200°, but slowly gives off carbonic anhydride at 300°. (H. Rose.)

Ammonio-carbonate of Zinc, $NH^3.Zn^2CO^3$, or *Carbonate of Zinc and Zinc-ammonium*, $\left.\begin{matrix}(CO)''\\ Zn.NH^3Zn\end{matrix}\right\}O^2$.—Deposited in crystals from a solution of precipitated carbonate of zinc in a strong solution of carbonate of ammonium. (Favre, *Traité de Chimie par Pelouze et Frémy*, 2^me^ éd. iii. 47.)

Carbonate of Zinc and Potassium. $(Zn^{12}K^8H^2)C^{11}O^{33} + 7aq.$—Deposited in crystals from a solution of chloride of zinc mixed with sesquicarbonate of potassium. (Deville, Ann. Ch. Phys. [3] xxxiii. 75.)

Carbonate of Zinc and Sodium. $(Zn^{16}Na^6)C^{11}O^{33} + 8aq.$—Small shining crystals, apparently tetrahedrons and octahedrons, obtained in like manner. (Deville.)

CARBONATE OF ZIRCONIUM. Solutions of zirconium-salts, treated with excess of alkaline carbonate, yield a precipitate soluble in acid carbonates of alkali-metal, and containing, according to Hermann, 76·6 per cent. zirconia and 20·39 per cent. water, agreeing with the formula $2Zr^4O^3.CO^2 + 6aq.$ According to Klaproth, however, it contains 51·5 per cent., and, according to Vauquelin, 55·5 per cent. zirconia.

CARBONIC ACID and **ANHYDRIDE.** See CARBON, OXIDES OF (p. 770).

CARBONIC ETHERS. *Carbonates of Alcohol-radicles.*—These compounds are metacarbonates, M^2CO^3, in which one or both atoms of base are alcohol-radicles. Those which contain 2 at. of alcohol-radicle, the *neutral carbonic ethers*, are obtained: 1. By the action of carbonate of silver on the iodides of the alcohol-radicles.—2. By the action of potassium or sodium on the corresponding oxalates. This reaction is attended with evolution of carbonic oxide, and probably takes place in the manner represented by the following equation:

$$\underset{\text{Oxalate of ethyl.}}{2(C^2H^5)^2C^2O^4} + K^2 = \underset{\text{Carbonate of ethyl.}}{(C^2H^5)^2CO^3} + \underset{\text{Ethylate of potassium.}}{2C^2H^5KO} + 3CO.$$

3. By the action of water on the chlorocarbonates of the alcohol-radicles (produced by passing oxychloride of carbon into the alcohols), and by the dry distillation of these same products. In presence of water, the action is such as is represented by the equation,

$$\underset{\text{Chlorocarbonate of amyl.}}{2\left(\left.\begin{matrix}\overset{''}{CO}\\ C^2H^5\end{matrix}\right\}\begin{matrix}O\\ Cl\end{matrix}\right)} + H^2O = \underset{\text{Carbonate of amyl.}}{(C^5H^{11})^2CO^3} + CO^2 + 2HCl.$$

The decomposition of the chlorocarbonates by dry distillation is more complicated, a considerable quantity of charred matter remaining behind; but the principal reaction is doubtless the splitting up of 2 at. of the chlorocarbonate into a carbonic ether and oxychloride of carbon, *e. g.*:

$$2(CClO^2.C^5H^{11}) = (C^5H^{11})^2CO^3 + COCl^2.$$

The neutral carbonic ethers are ethereal oily liquids, insoluble in water, soluble in alcohol and ether. They are decomposed by alcoholic potash, yielding carbonate of potassium and the corresponding alcohols. Two volumes of the vapour of each of these ethers contain two volumes of alcohol-radicle, a fact which tends to establish the dibasicity of carbonic acid. (See ACIDS, p. 46.)

The *acid carbonic ethers* (carbonates of alcohol-radicles and hydrogen) are not known, but some of their salts have been prepared.

CARBONATE OF ALLYL. $C^7H^{10}O^3 = (C^3H^5)^2CO^3$.—Obtained by the action of iodide of allyl on carbonate of silver (Zeise, Ann. Ch. Pharm. xcvi. 361), or of potassium or sodium on oxalate of allyl (Cahours and Hofmann, Phil. Trans. 1857, p. 555). It is an ethereal liquid lighter than water. The alcoholic solution treated with hydrate of barium, yields carbonate of barium and allyl-alcohol.

CARBONATE OF AMYL. $C^{11}H^{22}O^3 = (C^5H^{11})^2CO^3$.—Prepared: 1. By saturating amylic alcohol with oxychloride of carbon, decomposing the product with water, treating it with oxide of lead to remove chlorine, drying over chloride of calcium, and rectifying (Medlock, Chem. Soc. Qu. J. i. 368).—2. By decomposing oxalate of amyl with potassium or sodium. The action begins immediately, but heat is required to complete it. By distillation, a yellow liquid is obtained, which begins to boil at 130° C., yielding amylic alcohol; afterwards carbonate of amyl passes over at 225°, the quantity amounting to about three-fourths of the original distillate. The residue contains a strong-smelling viscid matter. (Bruce, Chem. Soc. Qu. J. v. 132.)

Carbonate of amyl is a colourless liquid, having an agreeable odour, and specific gravity = 0·9144; it boils at 224°—225° C.

CARBONATE OF ETHYL. *Carbonic Ether.* $C^5H^{10}O^3 = (C^2H^5)^2CO^3$.—This ether is prepared: 1. By the action of potassium or sodium on oxalate of ethyl, the materials being heated in a retort to 130° C., and fresh potassium or sodium added, as long as carbonic oxide continues to escape. On cooling the residue and treating it with water, carbonate of ethyl rises to the surface: it is dried with chloride of calcium, and rectified over a small quantity of sodium, then heated alone till the boiling point becomes stationary, the portion which afterwards passes over being collected apart (Ettling, Ann. Ch. Pharm. xix. 17).—2. By distilling a mixture of ethyl-carbonate and ethyl-sulphate of potassium. (Chancel, Compt. rend. xxxi. 521.)

$$C^2H^5.K.CO^3 + C^2H^5.K.SO^4 = K^2SO^4 + (C^2H^5)^2CO^3.$$

Carbonate of ethyl is a colourless limpid oil, having a sweet ethereal odour, and burning taste. Specific gravity = 0·975 at 19° C. Boils at 125°, and volatilises without decomposition. Vapour-density = 4·243 (Ettling); 4·09 (Cahours); by calculation for a condensation to 2 vol. it is $\frac{60 + 10 + 48}{2} \times 0·0693 = 4·089$. It is inflammable, and burns with a blue flame. It is insoluble in water, but dissolves easily in alcohol and ether. With alcoholic potash, it yields alcohol and carbonate of potassium. Heated with sodium, it gives off carbonic oxide, and forms ethylate of sodium, together with carbonate (?) (Löwig, Pogg. Ann. l. 122). The reaction is perhaps: $C^5H^{10}O^3 + Na = 2C^2H^5NaO + CO$ (Gm. ix. 393). Chlorine decomposes carbonate of ethyl, abstracting hydrogen, and forming the two following substitution-products:

Tetrachlorocarbonic Ether, $C^5H^6Cl^4O^3$, commonly called *Bichlorocarbonic ether.*—Obtained by passing chlorine through carbonate of ethyl in diffused daylight, heating the liquid to 70°—80° C. in the latter part of the process, and expelling the excess of chlorine by a stream of carbonic anhydride. It is a colourless liquid having a saccharine odour, much heavier than water, and insoluble therein; soluble in alcohol. It is decomposed by dry distillation. (Cahours, Ann. Ch. Phys. [3] ix. 201.)

Perchlorocarbonic ether, $C^5Cl^{10}O^3$. (Cahours, *loc. cit.*; Malaguti, Ann. Ch. Phys. [3] xvi. 30.)—Produced by the continued action of chlorine on the preceding compound in direct sunshine. The resulting crystalline mass must be purified by pressing it between folds of bibulous paper, washing it rapidly with small quantities of ether, again pressing, and leaving it for some days in a dry vacuum. It cannot be purified by crystallisation from alcohol or ether.

It is a white mass, composed of small needles, and having a faint odour; melts between 86 and 88° C., and solidifies between 65° and 63°. At a higher temperature it partly distils unaltered, and is partly resolved into carbonic anhydride, chloride of trichloracetyl, and trichloride of carbon:

$$C^5Cl^{10}O^3 = CO^2 + C^2Cl^3O.Cl + C^2Cl^6.$$

When dissolved in alcohol, it changes to an oil which is a mixture of carbonate and trichloracetate of ethyl, a large quantity of hydrochloric acid being produced at the same time:

$$C^5Cl^{10}O^3 + 4C^2H^6O = (C^2H^5)^2CO^3 + 2(C^2H^5.C^2Cl^3O^2) + 4HCl.$$

Heated with potash-ley, it yields formate, chloride and acid carbonate of potassium, together with hydrochloric acid:

$$C^5Cl^{10}O^3 + 10KHO = 2CHKO^2 + 5KCl + 5HCl + 3KHCO^3.$$

With gaseous ammonia, it forms sal-ammoniac, chlocarbethamide (trichloracetamide, according to Gerhardt, *Traité*, i. 16·6), and an unknown substance, which crystallises in long needles (Malaguti). When thrown into aqueous ammonia, it makes a hissing noise, like red-hot iron in water, and forms trichloracetamide, together with carbonate, formate, and chloride of ammonium, and probably also other ammoniacal salts. (Malaguti.)

Carbonate of Ethyl and Potassium. *Ethyl-carbonate* or *Carbovinate of of Potassium*, $C^3H^5KO^3 = C^2H^5.K.CO^3$. (Dumas and Péligot, Ann. Ch. Phys. [2] lxxiv. 6.)—Obtained by passing carbonic anhydride into a solution of perfectly dry hydrate of potassium in absolute alcohol, the liquid being carefully kept cool, which is best effected by introducing from time to time small portions of anhydrous ether. A crystalline deposit then forms, consisting of ethyl-carbonate of potassium, together with neutral and acid carbonate. The ethyl-carbonate is formed as represented by the equation:

$$C^2H^6O + KHO + CO^2 = C^2H^5.K.CO^3 + H^2O;$$

the acid carbonate results from the action of the water thus formed on a portion of the ethyl-carbonate, and the neutral carbonate from that of the excess of potash on the acid carbonate. To separate the ethyl-carbonate, the mass is treated with an equal volume of ether, which dissolves the excess of free potash, and leaves the two other salts undissolved: the ethyl-carbonate is then dissolved out by alcohol, precipitated by ether, and rapidly dried. It might doubtless be more easily prepared from anhydrous ethylate of potassium, C^2H^5KO.

Ethyl-carbonate of potassium is a white nacreous salt, which burns with flame on platinum-foil, leaving a carbonaceous residue, and yields by distillation an inflammable gas, a small quantity of ethereal liquid, and a residue of carbonate mixed with charcoal. Water transforms it into alcohol and acid carbonate of potassium:

$$C^2H^5.K.CO^3 + H^2O = C^2H^5.H.O + KHCO^3.$$

Ethyl-carbonic acid, $C^2H^5.H.CO^3$, has not yet been obtained; neither has *Carbonate of methyl*, $(CH^3)^2CO^3$, nor *Methyl-carbonic acid*, $CH^3.H.CO^3$.

Carbonate of Methyl and Barium. *Methyl-carbonate of Barium.* $CH^3.Ba.CO^3$ (Dumas and Péligot, *loc. cit.*)—A solution of anhydrous baryta in anhydrous methylic alcohol, subjected to the action of carbonic anhydride, yields a white precipitate, which after washing with methylic alcohol, consists entirely of methyl-carbonate of barium:

$$CH^3.H.O + Ba^2O + CO^2 = CH^3.Ba.CO^3 + BaHO.$$

The salt is insoluble in methylic or ethylic alcohol, but dissolves easily in cold water. The solution soon however becomes turbid, depositing a considerable quantity of carbonate of barium and giving off carbonic anhydride. The action is greatly assisted by a gentle heat, and at the boiling-point it is instantaneous.

Carbonate of Methyl and Ethyl. $C^4H^8O^3 = CH^3.C^2H^5.CO^3$ (Chancel, Compt. rend. xxxi. 521).—Obtained by distilling a mixture of methyl-carbonate and ethyl-sulphate of potassium:

$$CH^3.K.CO^3 + C^2H^5.K.SO^4 = K^2SO^4 + CH^3.C^2H^5.CO^3.$$

Carbonate of Phenyl and Hydrogen. $C^6H^5.H.CO^3$.—Salicylic acid (*q. v.*) may be regarded as constituted in this manner. When subjected to dry distillation, it splits up into carbonic anhydride and hydrate of phenyl.

Carbonate of Tetryl. *Carbonate of Butyl.* $C^9H^{18}O^3 = (C^4H^9)^2.CO^3$.—Produced: 1. By the action of iodide of tetryl on carbonate of silver, the materials (12 grammes of each) being enclosed together in a sealed flask, and heated for two days in the water-bath,—distilling the product, collecting apart that which passes over above 180° C., and rectifying (Ph. de Clermont, Ann. Ch. Phys. [3] xliv. 336).—2. By the action of chloride of cyanogen, either gaseous or liquid, on tetrylic alcohol, in presence of water. (Humann, *ibid.* xliv. 340):

$$2(C^4H^9.H.O) + CNCl + H^2O = (C^4H^9)^2CO^3 + NH^4Cl.$$

It is a colourless limpid liquid, lighter than water, and having an agreeable odour like that of carbonate of ethyl. It boils at 190° C. Aqueous ammonia converts it into tetrylic alcohol and carbonate of tetryl.

CARBONITROTOLUYLIC ACID, also called *Nitrodracylic acid.*—An acid crystallising in white slender needles, obtained by treating toluene with excess of strong nitric acid. Glenard and Boudault (Compt. rend. xix. 505), who discovered it, assigned to it the formula $C^8H^6NO^4$; it is more probably isomeric with nitrotoluylic acid, $C^8H^7NO^4$; or perhaps, as suggested by List (Gm. xiii. 24), the product was merely nitrobenzoic acid containing nitrostyrol.

CARBONYL. CO.—The diatomic radicle of the carbonates, carbamates, carbamides, &c.

CARBOPYRROLIC ACID. $C^5H^5NO^3 = \left.\begin{matrix}NH^2(C^5H^2O)''\\ H\end{matrix}\right\}O.$ (Schwanert, Ann. Ch. Pharm. cxiv. 63.)—An amic acid, obtained by heating Malaguti's pyromucamide, $C^5H^6N^2O$ (*q. v.*), which Schwanert regards as carbopyrrolamide, $N^2.H^4.(C^5H^2O)''$, with baryta-water in sealed tubes. Ammonia is then formed, together with carbopyrrolate of barium, $C^5H^4BaNO^3$, which crystallises in nacreous laminæ, and is not decomposed by heating with potash-ley. The concentrated aqueous solution treated with hydrochloric acid, deposits carbopyrrolic acid as a white crystalline precipitate. The *lead-salt*, $C^5H^4PbNO^3$. forms sparingly soluble nacreous laminæ.

When the aqueous solution of carbopyrrolic acid is heated to 60° C. or above, pyrrol, C^4H^5N, separates from it as a brown flocculent substance.

CARBOSTYRIL. $C^9H^7NO = N(C^8H^7)(CO)''$.—Produced by the action of sulphide of ammonium on nitrocinnamic acid. Probably an acid, $C^9H^9NO^2$, is first produced and afterwards converted into carbostyril by loss of 1 at. water, thus:

$$\underset{\text{Nitrocinnamic acid.}}{C^9H^7(NO^2)O^2} + 2H^2S = C^9H^9NO^2 + 2H^2O + S^2$$

$$\text{and}\quad C^9H^9NO^2 - H^2O = \underset{\text{Carbostyril.}}{C^9H^7NO.}$$

The liquid is supersaturated with hydrochloric acid, filtered, and evaporated. It then deposits crystals of carbostyril, coloured brown by a resin, which may be removed by recrystallising the product several times from boiling water.

Carbostyril forms beautiful colourless silky needles, moderately soluble in boiling water, easily in alcohol and ether; melts when heated, and at a higher temperature sublimes in shining needles; dissolves in hydrochloric acid, also in boiling potash, not in ammonia or in sulphuric acid. Heated with solid potash, it yields an oil which appears to be a peculiar alkaloïd (C^8H^7N ?) Boiled with oxide of silver, it forms a compound insoluble in boiling water, from which it is separated by acids in its original state. (Chiozza, Compt. rend. xxxiv. 598.)

CARBOTHIACETONINE. $C^{10}H^{18}N^2S^2$.—The sulphydrate of this base is deposited in yellow crystals on mixing acetone with ammonia and sulphide of carbon:

$$3C^3H^6O + CS^2 + 2NH^3 = C^{10}H^{18}N^2S^2 + 3H^2O.$$

(Städeler, Pharm. Centr. 1853, p. 433; see also Acetone, p. 28.)

CARBOTHIALDINE. $C^5H^{10}N^2S^2$.—A colourless crystalline body, produced by adding sulphide of carbon to an alcoholic solution of aldehyde-ammonia. It is insoluble in cold water and in ether, sparingly soluble in cold alcohol, easily in boiling alcohol. Dissolves in hydrochloric acid, and is reprecipitated by ammonia. Boiled with excess of hydrochloric acid, it is resolved into sulphide of carbon, sal-ammoniac, and aldehyde. On adding oxalic acid and then ether to the alcoholic solution of carbothialdine, crystals of oxalate of ammonium are formed. The alcoholic solution forms, with *nitrate of silver*, a greenish-black precipitate, which gradually changes into sulphide of silver; with *mercuric chloride* it forms a thick white curdy precipitate, and with *copper-salts* a green precipitate. (Redtenbacher and Liebig, Ann. Ch. Pharm. lxv. 43.)

CARBOTRIAMINE. $N^3\left\{\begin{matrix}\overset{''''}{C}\\ H^5\end{matrix}\right.$—Guanidine, a base obtained by the action of oxidising agents on guanine, may be viewed as a triple molecule of ammonia (N^3H^9), in which 4 at. H are replaced by the tetratomic radicle carbon. Several substitution derivatives of carbotriamine are also known, viz.:

Carbomethyltriamine. $N^3.\overset{''''}{C}.(CH^3)H^4$.—This constitution may be ascribed to methyluramine, a base resulting from the action of oxidising agents on creatine.

Carbotriethyltriamine. $N^3.\overset{''''}{C}.(C^2H^5)^3H^2$.—Produced by heating cyanurate of ethyl with ethylate of sodium. (Hofmann, Proc. Roy. Soc. xi. 282.)

Carbodiphenyltriamine. $N^3.\overset{''''}{C}.(C^6H^5)^2.H^3$.—This is the composition of melaniline.

Carbotriphenyltriamine. $N^3.\overset{''''}{C}.(C^6H^5)^3.H^2$.—This base is produced by the action of tetrachloride of carbon on phenylamine (p. 765).

All these bases may likewise be regarded as diamines containing 1 at. cyanogen in place of 1 at. hydrogen; thus, carbotriamine = cyan-diamine = $N^2(CN).H^5$. (See Ethyl-, Methyl-, and Phenyl-Diamines and Triamines.)

CARBOVINIC ACID. Syn. with Carbonate of Ethyl and Hydrogen. (See Carbonic Ethers, p. 801).

CARBOVINOMETHYLIDE. Carbonate of Ethyl and Methyl (p. 801).

CARBUNCLE. A gem highly prized by the ancients, probably the almandin or noble garnet.

CARBUREIC ACID. Syn. with Allophanic Acid.

CARBYL, SULPHATE OF. $C^2H^4S^2O^6$.—Syn. with Ethionic Anhydride.

CARDAMINE AMARA. The dried herb of this plant contains an azotised and sulphuretted organic acid, either identical with or very similar to the myronic acid of black mustard seed, in combination with an organic (probably basic) compound. Moreover this acid, either free or in combination with bases, develops, under the influence of myrosyn, but not under that of the emulsion of bitter almonds, an acrid volatile oil, very much like oil of horse-radish or scurvy grass. The decided bitterness and lower degree of pungency of the fresh herb appear to be due to the absence of myrosyn or of some analogous compound capable of developing the pungent oil. (Winckler, Jahrb. pr. Pharm. xviii. 89.)

CARDAMOM OIL. An essential oil extracted by distillation from the seeds of several kinds of cardamom, especially *Alpinia cardamomum* and *Amomum repens.* It is pale, aromatic, and has a burning taste. Specific gravity, 0·945. Soluble in ether, alcohol, and oils, also in acetic acid and caustic potash. It detonates with iodine, and is set on fire by strong nitric acid. The oil amounts to 4·9 per cent. of the seed-kernels of amomum repens.

Crystals deposited from old cardamom oil were found by Dumas and Peligot (Ann. Ch. Phys. [2] lvii. 334) to have the formula of a hydrate of camphene, $C^{10}H^{16}.3H^2O$.

Cardamom also contains a fixed non-drying oil, which has a rancid bitter taste, and saponifies by boiling with potash.

CARDOL. An oily liquid contained, together with anacardic acid (p. 209), in the pericarp of the cashew-nut (*Anacardium* or *Cassuvium occidentale*). To obtain, it the pericarp is exhausted with ether, the ether distilled off, the residue washed with water to remove tannin, then dissolved in 15 to 20 pts. of alcohol, and digested with recently precipitated hydrate of lead, which takes up the anacardic acid, while the cardol remains in solution. The greater part of the alcohol is removed from the filtered liquid by distillation, water added to the remaining liquid till it becomes turbid, and afterwards acetate and subacetate of lead till it is decolorised. Lastly, the lead is precipitated by sulphuric acid.

Cardol is a yellow oily liquid, insoluble in water, very soluble in alcohol and ether; the solutions are neutral to litmus. It is not volatile, but decomposes when heated. It blisters the skin strongly. According to Städeler, it contains 60 per cent. carbon and 8·8 or 8·9 hydrogen, whence he deduces the formula $C^{42}H^{31}O^4$; it should perhaps be $C^{21}H^{30}O^2$.

Cardol precipitates basic, but not neutral acetate of lead. Strong sulphuric acid dissolves it with red colour. Nitric acid appears to form with it under certain circumstances, the same products as with anacardic acid. Strong potash-ley colours it yellow, and ultimately dissolves it; and the solution, in contact with the air, acquires a deep red colour, and then forms red or violet precipitates with most metallic salts. (Städeler, Ann. Ch. Pharm. lxiii. 137.)

CAREX. The ashes of *Carex remota* and *C. acuta* have been examined by E. Witting. (J. pr. Chem. lxix. 149.)

The fresh plants contained in 100 pts.:

	Water.	Organic matter.	Ash.
Carex remota	52·75	45·18	2·07
„ *acuta*	69·60	29·28	1·12

The ash contained:

	KCl	NaCl	K^2O	Na^2O	Ca^2O	Mg^2O
C. remota . .	2·81	10·23	23·52	0·72	7·86	9·22
C. acuta . .	4·90	7·28	37·94	0·35	7·90	7·36
	Fe^4O^3	Mn^2O	P^2O^5	SO^3	CO^2	SiO^2
C. remota . .	2·23	1·45	4·95	1·93	4·75	30·33
C. acuta . .	1·39	2·02	7·66	1·36	4·86	16·98

The quantities of soluble and insoluble constituents of the ash were as follows:—

Soluble in water.	Soluble in nitric acid.	Insoluble.
49·15	29·45	21·40
57·56	31·59	10·85

CARICA PAPAYA. *Papaw Tree.*—Every part of the papaw tree, except the ripe fruit, affords a milky juice, which is used in the Mauritius as an effectual remedy for the tape-worm. In Europe, however, whither it has been sent in the concrete state, it has not answered. The milky juice is said to make meat washed in it very tender, and the leaves and fruit are said to have the same effect upon the flesh of old hogs and poultry which are fed with them; the flesh, however, soon becomes putrid. The juice yields a substance resembling the flesh or fibre of animals. U.

CARIES. See Bone (p. 623).

CARINTHIN. A sub-species of augite. Colour black. Occurs massive and disseminated. Internally splendent. Resino-vitreous. Distinct cleavage of 124° 34′. Fracture conchoïdal. Greenish-black variety: translucent on the edges, velvet-black, opaque. Occurs on the Saualp in Carinthia, in a bed of primitive rock, associated with quartz, kyanite, garnet, and zoisite. (*Jameson's Mineralogy.*) U.

Dana (ii. 172) enumerates it as a variety of hornblende.

CARMIDINE. An organic base produced by passing lutidine over red-hot lime. Its composition has not been ascertained. It produces a fine red colour with pine-wood and hydrochloric acid, and pale green with bleaching powder; hence it is probably a mixture of pyrrhol and vertidine. (Gr. Williams, Chem. Soc. Qu. J. vii. 97.)

CARMINAPHTHA. $C^{10}H^{6}O^{3}$ (?)—A red colouring matter obtained by heating naphthalene with a solution of acid chromate of potassium, and adding sulphuric or hydrochloric acid. It is dissolved by alkalis and precipitated in its original state by acids. (Laurent, Rev. scient. xiv. 560.)

CARMINDIN. A product which Laurent obtained by the action of ammonia on dibromisatin. (See Isatin.)

CARMINE. CARMINIC ACID. (Pelletier and Caventou, Ann. Ch. Phys. [2] viii. 250, li. 194; Warren de la Rue, Ann. Ch. Pharm. lxiv. 1, 23; Gerh. iii. 750.)—The colouring matter of cochineal (*Coccus cacti*). To separate it, cochineal is exhausted with boiling water; the extract is precipitated by subacetate of lead slightly acidulated, care being taken not to add the lead-solution in excess; the precipitate is washed with distilled water till the wash-water no longer gives a precipitate with a solution of mercuric chloride, then decomposed by sulphuretted hydrogen; the filtrate is evaporated to a syrupy consistence and dried over the water-bath; and the dark purple product thus obtained is treated with alcohol, which extracts the carminic acid.

This acid forms a purple mass, fusible and soluble in all proportions in water and in alcohol. Sulphuric and hydrochloric acid dissolve it without alteration. It bears a heat of 136° C. without decomposition. It is very hygroscopic. Its solution forms red precipitates with the alkaline earths, also with the acetates of lead, zinc, copper, and silver.

According to De la Rue's analysis, carminic acid contains 54·1 per cent. carbon and 4·6 hydrogen, agreeing nearly with the formula $C^{14}H^{14}O^{8}$.

Schützenberger (Ann. Ch. Phys. [3] liv. 52) regards De la Rue's carminic acid as a mixture, and assigns to pure carminic acid the formula $C^{9}H^{8}O^{5}$; he states also that it is mixed in cochineal with an oxycarminic acid, $C^{9}H^{8}O^{7}$, and perhaps also with other acids of intermediate composition. These statements do not appear, however, to be borne out by the results of his analyses.

Carminic acid is decomposed by chlorine and bromine. The bromine-compound is yellow and soluble in alcohol.

Carminic acid treated with nitric acid yields *nitrococcusic acid;* a compound which is isomeric with trinitranisic acid, and crystallises in yellow rhomboïdal tables, soluble in cold but more soluble in hot water; soluble also in alcohol and ether. All its salts are soluble in water.

The mother-liquor of the preparation of carminic acid contains a crystalline substance, insoluble in alcohol and ether, soluble in ammonia, and identical with *tyrosine.* (Warren de la Rue.)

The colouring principle of cochineal (carmine) was previously obtained in an impure state by Pelletier and Caventou (Ann. Ch. Phys. viii. 250), by treating the cochineal with ether to extract the fatty matter, and digesting the residue in alcohol.

The fine red pigment known in commerce as carmine, is prepared by treating a solution of cochineal with cream of tartar, alum, or acid oxalate of potassium. The fatty and albuminous matters then coagulate and carry down the colouring matter with them.

By treating a solution of cochineal with an alkaline carbonate and alum, a compound of the colouring matter with alumina is obtained, known by the name of *carmine-lake.*

For this purpose, the coarser sediment deposited from a decoction of cochineal, after the finer particles have been separated by decantation, is generally used. For cheaper sorts, extract of Brazil wood is sometimes mixed with the cochineal.

Cochineal colours are used for dying wool and silk crimson or scarlet; but the colours it produces are remarkable more for brilliancy than for durability, and are easily stained by water or alkalis. The mordants used are alum, cream of tartar, and tin-salt. (See *Ure's Dictionary of Arts, Manufactures and Mines*, i. 616.)

CARMINITE, or *Carmine-spar.*—A mineral, probably consisting of anhydrous arsenate of lead and iron, from Hornhausen in Saxony, where it occurs, with Beudantite, in quartz and brown iron ore. It occurs in clusters of fine needles, and in spheroïdal forms with columnar structure, cleaving parallel to the faces of a rhombic prism. Hardness = 2·5. Lustre vitreous, but pearly on the cleavage faces. Colour carmine to brick-red; powder reddish-yellow. Translucent. Brittle. Before the blowpipe it gives the reactions of arsenic, lead, and iron. (Dana, ii. 410.)

CARMUFELLIC ACID. An acid obtained by Muspratt and Danson (Phil. Mag. [4] ii. 293), by the action of nitric acid on the aqueous extract of cloves. It separates from the concentrated solution in yellow micaceous scales; and by precipitation with acetate of lead, decomposition of the lead-precipitate with sulphuretted hydrogen, and evaporation, it may be obtained in white crystals. It is insoluble in alcohol, ether, and cold water, soluble in hot water, ammonia, and potash. When heated, it yields a yellow oil and emits an odour of burnt sugar. Strong sulphuric acid does not act upon it in the cold, but carbonises it when heated. A moderately concentrated solution of the acid precipitates the salts of the alkaline earths, forming a very thick gelatinous mass. With copper-salts it forms a green, with silver and ferrous salts a white, and with ferric salts a yellow precipitate, all of flocculent character.—Muspratt and Danson assign to the barium and lead-salts of this acid, the doubtful formula, $C^{34}H^{30}MO^{33}$.

CARNALLITE. $KCl.2MgCl.6H^2O$.—A salt which sometimes separates in coarse-grained masses, often coloured by oxide of iron, from the mother-liquor of rock-salt, also of certain brine-springs; it may also be obtained by careful evaporation of the mother-liquor of sea-water. (Jahresber. d. Chem. 1856, p. 884; 1858, p. 739.)

CARNAUBA WAX. A wax which coats the leaves of the *Corypha cerifera*, a palm growing in Brazil, and is obtained by drying the leaves and melting the coating, which separates in scales. It forms hard, brittle lumps of yellowish-white colour, inclining to green, and has an odour of melilot, but no taste. It melts at 97° C., or according to Lewy (Ann. Ch. Phys. [3] xiii. 438) at 83·5°. According to Brande (Phil. Trans. 1811, p. 261), it is insoluble in cold, sparingly soluble in hot alcohol, forming a greenish solution. Similarly with ether. With fixed oils it mixes in all proportions. With caustic potash it forms a pale rose-coloured mass without actually saponifying. Nitric acid converts the wax into a yellow friable mass. Chlorine bleaches it. In other respects it behaves like beeswax. According to Lewy, it contains 80·3 per cent. carbon and 13·0 hydrogen. (Handw. d. Chem. 2te Aufl. ii. [2] 807.)

CARNAT. A variety of lithomarge from Rochlitz. (Breithaupt.)

CARNELIAN. A subspecies of chalcedony, of white, yellow, brown, and red colour. It has a conchoïdal fracture. Specific gravity 2·6. Semitransparent, with glistening lustre. The finest specimens come from Cambay and Surat in India. It is found in peculiar strata, thirty feet below the surface, in nodules of a blackish-olive colour, passing into grey. These, after two years' exposure to the sun, are boiled for two days, and thereby acquire the lively colours for which they are prized in jewellery. Carnelian is softer than common chalcedony. It consists mainly of silica (about 94 per cent.) with alumina, and a small quantity of sesquioxide of iron. According to Gauthier de Claubry, the colour proceeds, not from oxide of iron, but from an organic substance. This, however, is denied by Heintz. (Pogg. Ann. lx. 519.)

CAROLATHIN. A mineral containing organic matter, found in a coal-mine in Upper Silesia. It has the aspect of honey-stone; colour, honey-yellow to wine-yellow: translucent on the edges; has a faint unctuous lustre; very brittle. Specific gravity 1·515. Hardness 2·5. It is decomposed by hydrochloric acid. It contains about 15·10 per cent. water, 47·25 alumina, 29·52 silica, and 1·33 carbon. The water is not completely given off below 290° C., at which temperature the organic matter begins to decompose. The organic matter appears to be allied to humic acid. (Sonnenshein, J. pr. Chem. lx. 268.)

CAROTIN. $C^{18}H^{24}O$.—The colouring matter of the carrot (*Daucus Carota*). It was first isolated by Wackenroder in 1831 (Geiger's Mag. xxxiii. 144), afterwards examined by Zeise (J. pr. Chem. xl. 297), and recently with greater exactness by Husemann (Ann. Ch. Pharm. cxvii. 200).

Carrots also contain a colourless substance, hydrocarotin, $C^{18}H^{30}O$, containing 6 at. H more than carotin; and as they are colourless in the early stages of their growth, Husemann considers it probable that they at first contain only hydrocarotin, which gradually changes to red carotin by oxidation.

Preparation.—The expressed juice of bruised carrots is precipitated with sulphuric acid, to which a small quantity of tincture of galls is added; the half-dried coagulum is repeatedly boiled with five or six times its volume of 80 per cent. alcohol, which extracts the hydrocarotin; the residue, after drying at a gentle heat, is exhausted with sulphide of carbon; and the filtrate is mixed with an equal volume of absolute alcohol The solution, when left to itself, deposits the carotin in crystals of the dimetric system, which, while in the liquid, exhibit a golden-green lustre by reflected light; if, however, the sulphide of carbon was mixed with much alcohol, or if the solution was too much concentrated, the crystals are microscopic, and of a ruby-colour. The crystals are washed on a water-bath funnel with boiling 80 per cent. alcohol, afterwards with absolute alcohol, till the wash-liquid exhibits only a faint yellow colour, and when evaporated on a watch-glass, leaves small octahedral crystals.

The pure carotin which remains, exhibits, after drying in the air at mean temperature, a red-brown colour with velvet lustre, becoming bright red when dried at 100° C. It smells like Florentine violet-root, especially when heated. It is rather heavier than water; dissolves sparingly in alcohol, ether, and chloroform, easily in sulphide of carbon, benzene, and volatile oils; fixed oils dissolve it slowly, with red colour. It becomes soft at 126° C., and melts at 168° to a thick dark red liquid.

Carotin forms at low temperatures a colourless crystalline hydrate, which may be obtained by placing a concentrated solution of carotin in sulphide of carbon (not anhydrous) in a watch-glass, over a freezing mixture producing a temperature of $-10°$ C. It then separates as a white efflorescence made up of small needles; but as soon as it is taken out of the freezing mixture, it gives up its water, and is converted into red carotin. The same phenomenon is exhibited by a solution of carotin in benzene, excepting that the hydrate is then slightly yellow. Another hydrate is sometimes formed by adding to a dilute solution of carotin in sulphide of carbon, so much absolute alcohol, that the turbidity at first produced shall disappear, at least on heating the liquid. It separates in thin, iridescent, six-sided laminæ, and appears to be more stable than the first-mentioned hydrate. The composition of these hydrates has not been determined.

Carotin is very unstable; during the evaporation of its solution, it often separates in a light yellow amorphous modification, which is but sparingly soluble in sulphide of carbon. The red crystals gradually become colourless from without inwards, when exposed to daylight, and more quickly in sunshine; the new substance thus formed is inodorous, dissolves readily in alcohol or ether, but with difficulty in sulphide of carbon or benzene, and separates from these solutions in the amorphous state. The same change takes place when carotin is exposed for a long time to a heat of 150° C. Whether the new substance thus formed has the same composition as carotin, is not yet made out. Carotin heated to 250° C. forms a mobile liquid, which on cooling solidifies to a soft yellowish-red mass. At higher temperatures, it carbonises and gives off empyreumatic vapours.

Fuming nitric acid dissolves carotin with yellow colour, and water separates from the solution a yellow nitro-compound. *Strong sulphuric acid* dissolves carotin with purple colour; and on carefully adding water, the colour disappears, and a somewhat modified carotin separates in dark green flocks, which, like carotin altered by light, are coloured brown by sulphuric acid.—*Sulphurous anhydride* changes the colour of carotin to dark indigo, but does not alter it further; the blue substance crystallises from benzene in red cubes, and is also converted into red carotin by boiling with potash.

Dry chlorine gas converts carotin into tetrachloro-carotin, a white substance soluble in ether and in sulphide of carbon, becoming soft and dark-red at 100° C., melting at 120°. Another substitution-product containing less chlorine appears also to be formed.

Bromine and *iodine* likewise decompose carotin, forming substitution-products which are more fusible than carotin itself.

Carotin is not decomposed by dilute acids, by hydrochloric acid gas, sulphuretted hydrogen, sulphide of ammonium, or by alkalis, either in aqueous or in alcoholic solutions. Solutions of carotin are not precipitated by metallic salts; the alcoholic solution is coloured greenish by ferric chloride.

A substance having the same colour and composition as carotin, is obtained by treating tribromhydrocarotin, $C^{18}H^{27}Br^{3}O$, with potash; but the identity of the two has not yet been completely established. (See HYDROCAROTIN.)

CARPHOLITE. A silicate of manganese, aluminium, and iron, found near Schlackenwald in Bohemia, in radiated and stellated tufts, sometimes also in rhombic prisms of 111° 27′, and 68° 33′, with the lateral edges truncated. Specific gravity =

2·935. Hardness = 5 to 5·5. It is opaque, with straw-yellow or wax-yellow colour (hence the name, from *καρφος*, straw), and vitreous lustre. Its analysis gives—

SiO^2	Al^4O^3	Mn^4O^3	Fe^4O^3	Ca^2O	H^2O	F.		
37·53	26·47	18·33	6·27	—	11·36	—	= 99·961	(Steinmann).
36·15	28·67	19·16	2·54	0·27	10·78	1·40	= 98·97	(Stromeyer).
36·15	19·74	20·76	9·87	2·56	11·35	—	= 100·43	(Hauer).

Hence the formula $2R^4O^3.3SiO^2 + 3\,aq.$, the sesquioxides of aluminium, manganese, and iron being supposed to replace each other isomorphously.

By reducing the sesquioxides to protoxides (substituting $r = \frac{2}{3}R$), the formula becomes that of an orthosilicate, $2r^2O.SiO^2 + aq. = r^4SiO^4 + aq.$ According to Kobell, the manganese and iron are in the state of protoxides, and the formula is $(Mn^2O.Al^4O^3) + 2(H^2O.SiO^2)$. (*Rammelsberg's Mineralchemie*, p. 587.)

CARPHOSIDERITE. A hydrated phosphate of iron, containing small quantities of manganese and zinc, occurring in reniform masses and incrustations of straw-yellow colour and resinous lustre. Specific gravity 2·5; hardness 4 to 4·5. It is found in fissures in mica slate, and was first distinguished by Breithaupt, among some specimens from Labrador. (Dana, ii. 431.)

CARPHOSTILBITE. A straw-yellow variety of Thomsonite, from Bernflord, Iceland.

CARPOBALSAMUM. A commercial name of the volatile oil obtained from pimento, the fruit of *Myrtus pimenta.* It is yellowish, heavier than water, and smells like cloves.

CARROLITE. (W. L. Faber, Sill. Am. J. (2) xiii. 418; Smith and Brush, *ibid.* xvi. 366; Genth, *ibid.* xxiii. 115.)—A sulphide of cobalt and copper, from Finksburg, Carrol County, Maryland, U. S. Forms homogeneous, very friable masses, with indistinct cleavage; tin-white to steel-grey colour; metallic lustre; iron-black streak; uneven fracture, approaching to the conchoïdal. Hardness 5·5. Specific gravity 4·58. The mineral has not been found in distinct crystals, but appears to belong to the regular system.

S	As	Cu	Co	Ni	Fe	Quartz		
27.04	1·82	32·99	28·50	1·50	5·31	2·13	= 99·30	(Faber).
41·29	–	18·15	37·70	1·54	1·26	–	= 100·08	(Smith and Brush).
41·71	–	17·55	38·70	1·70	0·46	0·97	= 100·19	(Genth).

Faber deduces from his analysis (after deducting the nickel, arsenic, and iron, together with 3·468 per cent. sulphur required to form copper-nickel and magnetic pyrites), the formula $Co^2S.Cu^4S$ or CoCcuS. Smith and Brush regard the mineral as cobalt pyrites (Co^3S^2), in which part of the cobalt is replaced by copper.

CARRAGHEEN MOSS. See Caragheen Moss (p. 747).

CARROT. *Daucus Carota.*—The ashes of the root, leaves, and seed of the carrot have been analysed by Way and Ogston (Jahresber. f. Chem. 1849, Table E to page 656, and 1850, Table B to p. 660) with the following percentage results:

	White Belgian		Long red Surrey (on poor sandy soil)		
	Root.	Leaves.	Root.	Leaves.	Seed.
Potash	21·40—41·97	6·55— 7·53	43·73	17·10	16·21
Soda	8·18—17·53	9·46—12·76	12·11	4·85	1·23
Lime	6·08—11·89	29·50—34·98	5·64	24·04	32·96
Magnesia	3·20— 5·89	2·50— 3·23	2·29	0·89	5·70
Ferric oxide	0·59— 1·66	0·90— 4·06	0·51	3·43	0·84
Sulphuric anhydride	4·59— 9·49	5·47— 6·68	4·26	5·08	4·80
Silicic „	0·76— 1·92	1·83— 7·39	1·11	11·61	4·50
Carbonic „	15·15—19·11	14·92—22·25	18·00	23·15	15·13
Phosphoric „	7·86— 9·17	1·12— 2·55	12·31	6·21	13·38
Chloride of sodium	4·91— 7·65	8·77—15·11	trace	3·62	5·24
			99·96	99·98	99·99
Ash per cent. of dry substance	5·12— 8·80	15·80—21·30	5·44	10·03	4·30
„ fresh „	0·77— 1·06	2·85— 5·32	0·47	8·73	3·30
Moisture in 100 pts. of air-dried substance			86·40	80·00	13·00
Sulphur per cent. in dry substance			—	0·88	3·06

CARROT, OIL OF. The root of the carrot contains a very small quantity (0·0114) per cent. of a volatile oil, of specific gravity 0·8863 at 12° C., which may be obtained by distilling the fresh roots with water. It has a very strong pungent taste and smell, dissolves sparingly in water, freely in alcohol and in ether. (Wackenroder, Mag. Pharm. xxxiii. 145.)

CARTHAMIN. The colouring principle of safflower (*Carthamus tinctorius*), first examined by Chevreul, afterwards more fully by Schlieper (Ann. Ch. Pharm. lviii. 362.)

The flowers of *Carthamus tinctorius* contain two coloured principles, one yellow, soluble in water, and of no use in dyeing, the other red, soluble in alkalis and precipitable by acids from its alkaline solutions: this is *carthamin*. To prepare it, safflower is first washed repeatedly with water, to free it from the yellow substance, then treated with solution of carbonate of sodium; the liquid is saturated with acetic acid; and pieces of cotton are immersed in it, on which the carthamin is deposited. After twenty-four hours, the cotton is removed and treated with solution of carbonate of sodium, which redissolves the colouring matter; the solution is mixed with citric acid, whereby the carthamin is precipitated in red flocks; and, lastly, these flocks are dissolved in alcohol. The solution evaporated in vacuo yields the carthamin in the form of a powder, having a deep red colour with greenish iridescence. It is sparingly soluble in water, insoluble in ether, but easily soluble in alcohol, yielding a fine purple solution.

According to Schlieper, carthamin contains 56·9 per cent. carbon and 5·6 hydrogen, agreeing with the formula $C^{14}H^{16}O$.

The yellow colouring matter of carthamus is acid. It has a bitter taste and great colouring power. It combines readily with oxygen, and is converted into a brown substance. It unites with oxide of lead, forming the compound $(Pb^2O)^3.C^8H^{10}O^8$.

The red colouring matter of carthamus is used in dyeing, and for the preparation of rouge. The flowers, after being freed as much as possible from the yellow dye by repeated washing with water, are pressed and dried, and sent into the market in the form of cakes, known in commerce as *safflower*, *Spanish red*, or *China cake*.

For the preparation of rouge, the red colour is extracted by a solution of carbonate of sodium, and precipitated by sulphuric acid or by lemon juice previously depurated by standing. This precipitate is dried on earthen plates, mixed with talc or French chalk, reduced to a powder by means of the leaves of shave-grass triturated with it till they are both very fine, and then sifted. The fineness of the powder and proportion of the precipitate constitute the difference between the finer and cheaper rouge. It is likewise spread very thin on saucers, and sold in this state for dyeing.

Carthamus is used for dyeing silk or cotton of a poppy, cherry, rose, or bright orange-red. The cakes of safflower having been disintegrated by steeping in water, the red fibre is washed in sieves as long as the water which runs through acquires a yellow colour. It is then put into a deal trough, and sprinkled at different times with pearl ashes, or rather soda, well powdered and sifted, in the proportion of 6 lbs. to 100, mixing the alkali well as it is put in. The alkali should be saturated with carbonic acid. The carthamus is then put on a cloth in a trough with a grated bottom, placed on a larger trough, and cold water poured on till the larger trough is filled; and this treatment is repeated, with addition of a little more alkali toward the end, till the carthamus is exhausted and become yellow. Lemon juice or sulphuric acid is then poured into the bath, till it is turned of a fine cherry colour, and after it is well stirred, the silk is immersed in it. The silk is wrung, drained, and passed through fresh baths, washing and drying after every operation, till it is of a proper colour; after which it is brightened in hot water and lemon juice. For a poppy or fire colour, a slight annotto ground is first given; but the silk should not be alumed. For a pale carnation, a little soap should be put into the bath. All these baths must be used as soon as they are made, and cold, because heat destroys the colour of the red fecula. The colours produced by carthamus are very beautiful, but fugitive. (See *Ure's Dictionary of Arts, Manufactures and Mines*, i. 624.)

CARTILAGE. The cartilages consist of a dry flexible tissue, which contains but a small quantity of inorganic matter, and when boiled with water yields chondrin (*q. v.*), a substance resembling gelatin, but differing in certain reactions.

According to Scherer, the cartilage of the ribs contains 40·5 to 50·9 per cent. carbon, 7·0 to 7·1 hydrogen, 14·9 nitrogen, and 27·2 to 28·5 oxygen. (See BONE.)

CARVENE, CARVOL, and **CARVACROL.** (Völckel, Ann. Ch. Pharm. xxxv. 308; lxxxv. 246; Schweizer, *ibid.* l. 329; Gm. xiv. 283, 414.)—Essence of caraway consists of two essential oils, *carvene*, $C^{10}H^{16}$, and *carvol*, $C^{10}H^{14}O$, which may be separated by fractional distillation. The latter, however, is more easily prepared by agitating oil of caraway with an alcoholic solution of sulphide of ammonium: *sulphydrate of carvol*, $(C^{10}H^{14}O)^2.H^2S$ is then formed, and this compound, decomposed by ammonia yields carvol. (Varrentrapp, Handw. d. Chem. 2te Aufl. ii. [2] 812.)

Carvene is a colourless mobile oil, lighter than water, having a slight agreeable odour and aromatic taste. Boils at 73° C. It is nearly insoluble in water; very soluble in alcohol and ether; it absorbs hydrochloric acid, and forms a crystalline compound, which melts at 50·5 C. and consists of $C^{10}H^{16}.2HCl$.

Carvol is a liquid boiling at 250° C. Specific gravity 0·953. It is resinised by strong nitric or sulphuric acid, and forms with hydrochloric acid an oily compound containing $C^{10}H^{14}O.HCl$. *Sulphydrate of carvol*, $2C^{10}H^{14}O.H^2S$, crystallises from solution in alcohol in long needles having the lustre of satin; they are fusible, and when cautiously heated, sublime almost unaltered (Varrentrapp). *Sulphydrate of sulphocarvol*, $2C^{10}H^{14}S.H^2S$, is produced by passing sulphuretted hydrogen for a long time through alcohol in which the preceding compound is suspended. It then separates as a thick oil, which dissolves in ether, and is deposited therefrom in white flocks. The ethereal solution precipitates chloride of mercury and dichloride of platinum; but the precipitates have not a constant composition. (Varrentrapp.)

Carvacrol, a substance isomeric with carvol, is obtained by treating oil of caraway with potash, or again by treating the same oil with iodine, cohobating several times, and washing the product with potash; as thus obtained, however, it is mixed with carvene. Carvacrol is also found among the products of the action of iodine on camphor (p. 729), $C^{10}H^{16}O + 2I = 2HI + C^{10}H^{14}O$. Carvacrol when pure is a colourless viscid oil lighter than water, and soluble in water to a small amount. It has an unpleasant odour, and an acrid very persistent taste. Boils at 232° C., giving off vapours which irritate the organs of respiration. It burns with a bright very smoky flame.

CARYOPHYLLIC ACID. Syn. with Eugenic Acid.

CARYOPHYLLIN. $C^{10}H^{16}O$.—This substance, isomeric with common camphor, is contained in considerable quantity in *cloves*, the dried flower-buds of the clove-tree, *Caryophyllus aromaticus*, which is indigenous in New Guinea and the Moluccas, and cultivated in Sumatra, in the isles of Mauritius and Bourbon, and in Brazil. It may be extracted by treating cloves with cold alcohol; the liquid in about fifteen days becomes covered with crystals, which may be purified with solution of soda. The cloves may also be exhausted with ether, and the caryophyllin separated by agitating the ethereal solution with water. Crude oil of cloves also deposits caryophyllin on standing.

Caryophyllin forms silky colourless needles arranged in radiating groups, destitute of taste and smell. It melts with difficulty and with partial decomposition (Dumas); sublimes at about 2 5° C. (Muspratt). It dissolves sparingly in cold alcohol, easily in boiling alcohol and in ether; also in hot caustic alkalis. Strong sulphuric acid dissolves it in the cold without blackening, but the liquid blackens when heated. Nitric acid converts it into a resinous substance. (Gerh. iv. 278.)

CASCALHO. The alluvial soil, consisting of ferruginous sand and clay, in which Brazil diamonds are found.

CASCARILLA BARK. The bark of cascarilla, *Croton eleutheria* and *Cr. cascarilla*, shrubs indigenous in the West Indies. It contains albumin, tannin, a red colouring matter, a fatty substance, an essential oil having an agreeable odour, wax, resin, a gummy substance, starch, pectic acid, wood, fibre, and cascarillin, together with a calcium-salt and chloride of potassium. It possesses tonic and aromatic properties.

CASCARILLA, OIL OF. Cascarilla bark contains a volatile aromatic oil, amounting to 0·37 per cent. (Bley), 0·87 (Trommsdorf). It is dark yellow, sometimes with a bluish tinge; of specific gravity 0·909—0·938; boils at 180° C. or higher (Trommsdorf). According to Völckel, the first distillate is colourless, of specific gravity 0·862, and boils at 173° C. (Gm. xiv. 363.)

CASCARILLIN is obtained by treating the aqueous extract of cascarilla bark with acetate of lead, filtering, and precipitating the excess of lead with sulphuretted hydrogen. The liquid evaporated at a gentle heat deposits an amorphous mass, from which, after washing with cold alcohol, the cascarillin may be extracted by boiling alcohol. It is purified by recrystallising several times, after decolorising with animal charcoal. It crystallises in needles or in hexagonal plates, which are colourless, bitter, fusible, decomposible by heat, sparingly soluble in water, more soluble in alcohol, ether, hydrochloric acid, and sulphuric acid. The aqueous solution is not precipitated by alkalis, tannin, acetate, or subacetate of lead. (Duval, J. Pharm. [3] viii. 91.)

CASE-HARDENING. Steel when hardened is brittle, and iron alone is not capable of receiving the hardness which steel may be brought to possess. There is, nevertheless, a variety of articles in which it is desirable to obtain all the hardness of steel together with the toughness of iron. These requisites are united by the art of case-hardening, which does not differ from the making of steel, except in the shorter duration of the process. Tools, utensils, or ornaments intended to be polished, are first manufactured in iron and nearly finished, then put into an iron box, together with vegetable or animal charcoal in powder, and cemented for a certain time. This treatment converts the external part into a coating of steel, which is usually very thin, because the time allowed for the cementation is much shorter than when the whole is intended to be made into steel. Immersion of the heated pieces in water hardens the surface, which is afterwards polished by the usual methods. Moxon (*Mechanic Exercises*, p. 56) gives the following receipt: — Cow's horn or hoof is to be baked or thoroughly dried, and pulverised. To this add an equal quantity of bay salt: mix them with stale chamber ley, or white wine vinegar: cover the iron with this mixture, and bed it in the same in loam, or enclose it in an iron box: lay it then on the hearth of the forge to dry and harden: then put it into the fire, and blow till the lump have a blood-red heat, and no higher, lest the mixture be burnt too much. Take the iron out, aud immerse it in water to harden.

The same end is now more effectually attained by heating the tool red-hot, and sprinkling over it ferrocyanide of potassium (yellow prussiate) in fine powder, then quenching it in water. Some prefer smearing the surface of the bright iron with loam made into a thin paste, with solution of the yellow prussiate, drying it slowly, then heating it nearly to whiteness, and plunging it into cold water, when the heat has fallen to dull redness. (See *Ure's Dictionary of Arts, Manufactures and Mines*, i. 630.) U.

CASEIN constitutes the chief part of the nitrogenised matter contained in the milk of mammiferous animals. It takes its name from *caseus*, the Latin name of cheese, which is principally composed of casein mixed with fatty matters (butter) and decomposition products of casein (carbonate of ammonium and ammoniacal salts of acetic, butyric, valeric acids, &c.).

Preparation.—According to the views of Berzelius, Braconnot, and others, two modifications of casein are supposed to exist, the one *soluble* in water, the other coagulated and *insoluble* in water. *Soluble* casein has, however, never been prepared free from alkali, and is most probably identical with albuminate of potassium or sodium (Lehmann). *Insoluble* casein has nearly the same properties and composition as insoluble albumin.

Soluble casein may be prepared as follows: Fresh milk, from which the cream has been removed, is evaporated at a gentle heat, a portion of the casein becoming coagulated, while the rest remains dissolved. The residue is exhausted with ether, in order to extract fatty substances, and treated with water, which dissolves casein and lactin (sugar of milk); a little alcohol is next added to the aqueous solution, whereby most of the lactin is precipitated, the precipitate is washed with weak alcohol, and a solution of casein is obtained which always contains lactin and alkali. (Gerh. iv. 484.)

Insoluble casein may be obtained by simply heating creamed milk near to the boiling point, coagulating the liquid with a few drops of acetic acid, completely exhausting the coagulum with water, treating with alcohol and ether, drying and powdering the residue, and repeatedly digesting it with ether (Dumas and Cahours). Perhaps the best method is that of Bopp (Ann. Ch. Pharm. lxix. 16). Milk is coagulated with hydrochloric acid, the coagulum washed, first with distilled water, and then with water containing 2 or 3 per cent. hydrochloric acid, and finally with cold distilled water. A jelly is thus obtained, dissolving at 40° C. in a large quantity of water. This solution is filtered and carbonate of ammonium cautiously added, and the precipitate is well washed and exhausted with ether-alcohol. Whatever acid be employed in the coagulation, the casein, when treated in the manner described, never contains any trace of acid, and has always the same composition. (Gerh. *loc. cit.*)

Chemical Properties.—Soluble casein, when prepared in the manner described, leaves, after evaporation, an amorphous residue, inodorous, but having a sickly taste. It does not redissolve completely in water, nor does the solution coagulate by heat, but merely becomes covered with a film, which forms again as often as it is removed. Soluble casein is coagulated by alcohol, a portion at the same time entering into solution; a larger quantity is dissolved by boiling alcohol. The coagulum produced by *absolute* alcohol is completely insoluble in water. Solution of casein is precipitated by all *acids* (except carbonic acid); the precipitates redissolve in an excess of acid, and the solutions become covered with a film when evaporated in an open vessel. Mineral acids precipitate casein from its acetic acid solution. After the coagula thus obtained have been well washed with water, they still redden litmus, although they do not impart an acid reaction to water, even on boiling. The spontaneous coagulation of milk is due to the formation of lactic acid (produced by the fermentation of lactin) the acid neutralising the alkali in which the casein was dissolved, and thus rendering the casein insoluble.

Soluble casein always contains a large amount of mineral matter (when coagulated by alcohol, 8 to 10 per cent.). Casein coagulated by an acid yields from 1 to 5 per cent. ash, and the ash is never alkaline (Scherer). Casein contains phosphate of calcium as a constituent part. Mulder (Arch. f. 1828, p. 155) found in casein 6 per cent. phosphate of calcium, which is precipitated on coagulating any caseous liquid with an acid, although enough free acid be added to dissolve any uncombined phosphate of calcium.

When moist casein is exposed to the air, it soon begins to putrefy, yielding sulphide and carbonate of ammonium, a neutral oily body, having a disagreeable smell, together with butyric and valeric acids; at the same time the undecomposed casein dissolves in the ammonia formed (Iljenko, Ann. Ch. Pharm. lxiii. 264). According to Bopp, a crystalline body possessing a most powerful odour, is formed under the same circumstances. When casein putrefies out of contact with the air, it yields acetic, butyric, valeric, and capric acids, as well as ammonia.

The following are the results of the analysis of coagulated casein, deducting ash:

	Scherer.			Rochleder.	Walther.	Verdeil.
	By alcohol.	By the turning of milk.	By acetic acid.	By sulphuric acid.		
Carbon . .	53·7	54·0	53·8	53·8	—	—
Hydrogen . .	7·2	7·2	7·4	7·1	—	—
Nitrogen . .	15·6	15·7	15·7	—	—	—
Sulphur . .	—	—	—	—	1·0	0·9
Oxygen . .	—	—	—	—	—	—

	Dumas and Cahours.*					
	From cow's milk by acetic acid.	From goat's milk, by acetic acid.	From asses' milk, by acetic acid.	From sheep's milk, by acetic acid.	From human milk, by alcohol.	From blood by weak boiling alcohol †
Carbon . .	53·5	53·6	53·7	53·5	53·5	53·8
Hydrogen . .	7·1	7·1	7·1	7·1	7·1	7·1
Nitrogen . .	15·8	15·8	16·0	15·8	15·8	15·9
Sulphur . .	—	—	—	—	—	—
Oxygen . .	—	—	—	—	—	—

(Gerh. iv. 487.)

These numbers agree very closely with those obtained by the same chemists in the analysis of albumin, except that casein appears to contain less sulphur than albumin (2·16, Verdeil). Casein does not appear to contain any phosphorus, except in the form of phosphate of calcium.

Coagulated casein is readily soluble in caustic potash; after boiling, the solution contains sulphide of potassium. When casein is fused with caustic potash, ammonia is first evolved, then hydrogen; the mass, at first dark brown, gradually clears and becomes yellow; it is then completely soluble in water, and contains tyrosin, leucin, valerate (sometimes butyrate), and oxalate of potassium, as well as the potassium-salt of a volatile acid having an excrementitious odour (Liebig). If a very weak solution of alkali is saturated with casein, the alkaline reaction completely disappears; the solution thus obtained is precipitated by all acids except carbonic. Casein dissolves in a solution of phosphate of sodium, and neutralises it at the same time. It also dissolves largely in solutions of the alkaline carbonates, of common salt, chloride of ammonium, nitrate of potassium, &c. These solutions do not coagulate by heat, but become gradually covered with a film which is insoluble in dilute alkalis and acids. The same film is formed when milk is heated.

The solutions of casein are precipitated by all *earthy and metallic salts*. The precipitates with chloride, sulphate, and acetate of calcium and sulphate of magnesium, are thrown down only on heating the liquid. Compounds insoluble in water and hardening on exposure to the air, are obtained by heating casein with carbonate of calcium or of barium. The compound of casein and lime, prepared from clotted milk, is imputrescible, and is employed in distemper painting. (Gerhardt, *loc. cit.*)

If well washed casein, while still moist, be digested with water containing 0·0005 per cent. hydrochloric acid, it dissolves completely. The liquid, filtered from a trace of fat, deflects the rays of polarised light to the left, and has all the characteristics of a solution of albumin. (Bouchardat.)

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* The ashes varied between 1·5 and 5·4 per cent. The substance was dried 150° C.

† See "Physiological Sources of Casein." (p. 812.)

Ozone acts energetically upon casein, the casein being apparently first converted into a substance resembling albumin, which is again destroyed on prolonging the action of the ozone (Gorup-Besanez, Jahresb. d. Chem. 1858, p. 63). O. Maschke says that he obtained by this reaction a crystallised compound of casein with a new acid (*ibid.* p. 543). Concentrated *hydrochloric acid* turns casein blue or violet, forming the same products of decomposition as with albumin. *Tannin*, from gall-nuts, precipitates the most dilute alkaline solutions of casein. *Mercuric chloride* yields with soluble casein a bulky white precipitate, soluble in acetic acid and in excess of alcohol: the precipitate does not contain chlorine, and is probably identical with albuminate of mercury (Elsner). Soluble casein is also precipitated by *acetate* and *subacetate of lead*, by *alum*, *mercurous nitrate*, and *sulphate of copper*. The acetic acid solution of casein is moreover precipitated by *ferrocyanide*, *chromate*, and *iodate of potassium.*

Casein yields the same products as albumin with sulphuric acid and acid chromate of potassium or peroxide of manganese (Guckelberger). When chlorine is passed through ammoniacal solution of casein, a product is likewise obtained analogous to that produced in the same way from albumin.

The coagulation of milk by rennet (the mucous membrane of the fourth stomach of young calves), is supposed by Liebig to result from the animal matter acting as a ferment, and transforming the lactin of the milk into lactic acid; since milk coagulated by rennet at a temperature of 40° C. always has an acid reaction. It appears, however, that milk may be coagulated by rennet, even when rendered alkaline by the addition of small quantities of carbonate of soda, so that after coagulation the liquid still remains alkaline: it is only necessary to operate at a higher temperature (between 50° and 60° C.) (Gerh. iv. 490.)

Sources and physiological nature of Casein.—When morbid bile is evaporated, a film of coagulated mucus and of a caseous substance is formed (Frerichs, Hann. Ann. v. pp. 1 and 2). Moleschott (*Physiologie des Stoffwechsels*, Erlangen, 1851. p. 366, &c.) found casein in the fluid filling the interstices of *cellular tissue*, also in the interstitial fluid of the *neck-band*. M. S. Schultze found casein in the liquid impregnating the middle lining of the arteries: in 100 pts. of the dried fibrous lining membrane of the *aorta thoracica*, out of 17·4—23·1 pts. soluble constituents, 7·24 pts. casein; and in the middle lining of the *carotid*, which contains more contractile fibrous cells than the *aorta*, in 39 per cent. soluble pts. 21 pts. of casein were found. The juice of flesh appears to contain casein; at least this substance has been found in the liquid pressed from flesh. It is not certain that blood contains casein. Dumas and Cahours have extracted from the coagulum of blood, a substance which has the same composition as casein (see analysis of casein), but is soluble in warm alcohol (Ann. Ch. Phys. [3] vi. 416). Frerichs almost always observed in the soluble constituents of the contents of the *small intestine*, albuminous compounds sometimes having the properties of albumin, sometimes of casein. A substance resembling casein is extracted by boiling alcohol from the contents of the small intestine of the human fœtus, from the fifth to the sixth month (Lehmann). The presence of casein in the *chyle* is exceedingly improbable. (Lehm.)

When yoke of egg is treated with ether and water, a coagulum collects under the yellow stratum of ether. If, after removing the ether, the coagulum be filtered off and washed until the wash-water becomes only opaline by heat, a substance remains on the filter identical with casein prepared by Rochleder's or Bopp's method (Ann. Ch. Pharm. xiv. 253—6; Bopp, *ibid.* lxix. 16—37), only that it contains a little albumin poor in salts; the albumin was precipitated by diluting the yoke solution with water (Gmelin, *Handbuch*, viii. 2, 282). Casein has been said to exist in *urina chylosa.* Reveil says that the urine of a child twenty-two weeks old, collected in his presence, concontained all the constituents of milk. Lehmann and Chevalier were unable to confirm this statement. Lehmann does not deny that albuminoïdal substances may pass into the urine, but with their properties so changed as not to agree with those of any known albuminoïdal compound.

Coagulable albuminate is sometimes found in the discharge of *serous* skin. Casein is not contained in normal *pus*, nor has it been detected with certainty in abnormal pus.

The casein of *human milk* is stated by Simon to be yellowish-white and very friable; it absorbed moisture from the air, and was but incompletely precipitated by alum or by acetic acid, from its aqueous solution. Casein from *cow's milk* is less soluble in water, and becomes viscid and horny on drying. *Canine milk* gives a casein which does not become viscid and horny when dried, and is less soluble in water.

The following are the percentages of casein in milk from various sources. (Gmelin, Handb. viii. [2] 254, 5.)

HUMAN.	COW.	BITCH.	ASS.
3·37 (Clemm). 2·7—3·1 (Haidlen). *3·924 (Vernois and Becquerel).	3·0—3·4 (Boussingault) 4·16 average (Playfair). 5·52 (Vernois and Becquerel).	14·6 (Simon). 9·73—13·6 (Dumas). 11·69 (Vernois and Becquerel).	1·95 (Péligot). 1·70 Gubler and Quévenne). 3·57 (Vernois and Becquerel).
GOAT.	SOW.	SHEEP.	MARE.
4·52 (Payen). 6·03 (Clemm). 5·51 (Vernois and Becquerel).	8·45 (H. Scherer). 7·36 do. Essex sow.	15·3 (Stipriaan, Luiscius, and Bondt). 6·98 (Vernois and Becquerel).	16·2 (Luiscius and Bondt). 3·24 (Vernois and Becquerel).

The soluble casein of milk is rapidly coagulated by the gastric juice, and then gradually digested. Milk is the most indigestible of albuminous bodies. A dog digests 100 grammes of cheese in 3—3·5 hours; boiled casein in 7 hours. E. v. Schröder remarked that in the human stomach, 2·5 hours after fresh milk had been taken, casein still remained in the form of amorphous or filmy transparent lumps; and even after the lapse of 3½ hours, undissolved milk globules, adhering to small coagula of casein, were almost always found, although the greater part of the milk seemed to have passed from the stomach. Cheeses which are hard, fat, and poor in salts, are more difficult of digestion than loosely coagulated, moist, and fresh cheeses (Gmelin, Handb. iv. [2] 616). The digestibility of casein naturally depends upon its state of aggregation; the casein of human milk, which coagulates with great difficulty, is more readily digested than that of cow's milk, which is more viscid. C. E. L.

CASEIN, VEGETABLE. See LEGUMIN.

CASSAVA. *Mousache, Cassave, Cassava Bread*, is a kind of starch, obtained from the root of the *maniock* (*Jatropha manihot, L.*) in the West Indies, where this plant is indigenous. The root is grated to a pulp, which is strongly squeezed in bags by a press. The juice contains nearly one-half per cent. of an exceedingly poisonous matter, volatile, and therefore entirely dissipated by the heat on iron plates, to which the pressed and crumbled pulp is exposed. Of that poison, as obtained by distillation, 35 drops served to kill, with horrible convulsions, in six minutes, a negro who had been convicted of murder by poison. Cassava may be freed from woody particles by solution, filtration, and evaporation. If in this state it is exposed to heat on an iron plate, it concretes into mammellated small lumps, called *tapioca*, an agreeable food, which is often imitated by means of potato-starch.

Cassava flour may be distinguished, by the microscope, from arrow-root, potato-starch, and wheat-starch, by the shape of its particles, which are spherules of $\frac{1}{1000}$ of an inch in diameter, while those of the second and third farina are ellipsoids, varying in size; and those of the fourth are spherules, clustered more or less together. U.

CASSEL YELLOW. See LEAD, OXYCHLORIDE OF.

CASSIA CARYOPHYLLATA. The bark of *Dicyphellium caryophyllatum* (Nees), a lauraceous tree growing in Brazil. It has an agreeable taste of cloves, an aromatic odour, and contains, according to Trommsdorff, 19 per cent. resin, 8·0 tannin, 10 gum and phosphate of calcium, and 59 woody fibre. It also yields an aromatic volatile oil containing eugenic acid. (Handw. d. Chem. 2te Aufl. ii. [2] 820.)

CASSIA CINNAMONEA, *Cinnamon Cassia, Chinese Cassia bark*, is the bass or inner bark of *Cinnamonum aromaticum*, a lauraceous tree indigenous in China, and cultivated in Java. It has a burning taste and aromatic odour, and contains, according to Bucholz, 4·0 per cent. soft resin, 14·6 extractive matter, 64·3 woody fibre, and bassorin; volatile oil, &c. According to Mulder, it also contains tannic acid (Handwört.) By distillation with salt water, it yields *oil of cassia*, an oil mainly consisting of cinnamic aldehyde, and nearly identical with the oil obtained from Ceylon cinnamon.

CASSIA FISTULA. The fruit of *Bactyrilobium fistula*, a leguminous plant growing in India and in the interior of Africa. According to Vauquelin, it contains 14·8 per cent. sugar, and 1·5 gum, together with pectin, gluten, &c.; according to Caventou, it contains cassiin. The legume is divided into a number of transverse cells, filled with a sweet, slight acid pulp, 100 pts. of which contain, according to Henry:

	Sugar.	Gum.	Tannin.	Yellow colouring matter and mucus.	Water.
West Indian .	69·2	2·6	3·9	1·3	23·2
African . .	61·0	6·7	13·2	—	19·0

CASSIA BUDS. The undeveloped flowers of *Cinnamonum Louresii* (Nees). By distillation with salt water, they yield oil of cassia. (Handw.)

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* Casein and extractive matter: average of 89 persons (1·932—7·092).

CASSIIN. A bitter principle obtained from *Cassia fistula*. It is soluble in water and in alcohol, and is precipitated therefrom by sulphuric, nitric, or hydrochloric acid. (Caventou, J. Pharm. xiii. 340.)

CASSITERITE. Native oxide of tin. (See TIN.)

CASSITEROTANTALITE. Tantalite from Broddbo in Finland, containing oxide of tin. (See TANTALITE.)

CASSIUS, PURPLE OF. A purple compound of the oxides of gold and tin. (See GOLD.)

CASSONIC ACID. A syrupy uncrystallisable acid, obtained, together with oxalic and saccharic acid, by oxidising cane-sugar with nitric acid. It forms a speculum with nitrate of silver. The barium-salt appears to contain $C^6H^6Ba^2O^7$. (Siewert, Institut. xxi. 78.)

CASTELNAUDITE. A mineral from the diamond sands of Bahia in Brazil. It consists mainly of hydrated phosphate of yttrium, and occurs in imperfect crystals or irregular grains, probably trimetric, of greyish-white or pale yellow colour, unctuous adamantine lustre, harder than fluorspar, but scratched by a steel point. (Damour, Institut. 1853, p. 78.)

CASTILLOYA ELASTICA. A Mexican scrophulariaceous plant, which yields caoutchouc.

CASTINE. A crystalline basic substance, obtained from the seed of *Vitex Agnus castus, L.* It is bitter, insoluble in water, soluble in alcohol, ether, and acids; forms a crystalline hydrochlorate. (Landerer, Buchner's Repert. liv. 90.)

CASTOR. A variety of PETALITE (*q. v.*)

CASTOREUM. *Bibergeil.*—A substance found in a pair of small sacs situated in the genital organs of the beaver (*Castor Fiber* and *Castor americinus*). There are three sorts of it, Russian, Bavarian, and American or Canadian. Of these, the Russian is most valued, though the Bavarian is considered nearly equal to it. Castoreum when fresh, is soft and unctuous, but becomes hard and firm when dry; it has a black or brownish-black colour, and is somewhat shining. It has a peculiar pungent odour, and a bitterish spicy taste, which irritates the throat; it is used in medicine as an antispasmodic.

According to Brandes, Russian and Canadian castoreum differ considerably in composition, as shown by the following table:

Volatile oil	1·00	2·00
Castoreum resin	13·85	58·60
Cholesterin	—	1·20
Castorin	0·33	2·50
Albumin	0·05	1·60
Glutinous substance	2·30	2·00
Extract soluble in water and alcohol	0·20	2·40
Carbonate of ammonium	0·82	0·80
Phosphate of calcium	1·44	1·40
Carbonate of calcium	33·60	2·60
Sulphates of potassium, calcium, and magnesium	0·20	—
Gelatinous substance extracted by potash	2·30	8·40
Gelatinous substance, extractable by potash, soluble in alcohol	—	1·60
Membranes, skin, &c.	20·03	3·30
Water and loss	22·83	11·70
	98·95	100·10

Wöhler by distilling Canadian castoreum with water, obtained phenic acid, together with benzoic acid and salicin; he suspected also the presence of ellagic and salicylic acid. Lehmann found bile in fresh castoreum, by Pettenkofer's test; also alkaline sebates and urates, and an albuminoïdal substance. Laugier, Brandes, Batka, and Riegel, found benzoic acid. Lehmann found, as the mineral constituents of castoreum, a small quantity of chloride of sodium, sal-ammoniac, and other soluble salts, also phosphate of sodium and ammonium, and an abundance of phosphate of calcium and phosphate of magnesium.

A substance resembling castoreum is likewise secreted by the prepuce (*Præputium penis* and *clitoridis*) of man and of the horse. Lehmann gives the following table of the composition of: A. Fresh German castoreum; B. Smoked Russian; C. Canadian; D. *Smegma præputii* of the horse; E. of man:

	A.	B.	C.	D.	E.
Ethereal extract	7·4	2·5	8·2	49·9	52·8
Alcoholic extract	67·7	64·3	41·3	9·6	7·5
Water extract	2·6	1·9	4·8	5·4	6·1
Acetic acid extract	14·2	18·5	21·4	5·4	9·7
„ „ consisting of carbonate of calcium and albuminoïdal substance . .	2·4	3·4	5·8	2·8	5·6
Portions of skin	5·7	9·4	18·4	26·8	18·5
	100·0	100·0	99·9	99·9	100·2

The ethereal extracts contained saponifiable fats, cholesterin, and castorin, and a fat which became very finely divided in water.

Castoreum resin is obtained by evaporating the mother-liquor of castorin (*vid. inf.*) to dryness, exhausting the residue with water, then dissolving in alcohol, and evaporating. It is black-brown, shining, brittle, nearly insoluble in ether, soluble in aqueous alkalis, and precipitated therefrom by acids.

Castoreum-oil, obtained by distilling castoreum with water, is pale yellow, viscid, sparingly soluble in water, easily in alcohol, and has a sharp bitter taste. Russian castoreum yields 2 per cent. of this oil; Canadian 1 per cent. (Handw. d. Chem. 2te Aufl. ii. [2] 1034.)

CASTORIN. A fatty substance obtained from castoreum. A solution of castoreum in 6 pts. of alcohol saturated while warm, yields on cooling a deposit of ordinary fat, and the mother-liquor deposits crystals of castorin by slow evaporation. This substance, when purified by repeated crystallisation, forms delicate, transparent, four-sided needles, having a faint taste and smell of castoreum. It melts in boiling water, and solidifies on cooling to a hard translucent, pulverisable mass. It is but sparingly soluble in cold alcohol; ether dissolves it readily; volatile oils only when warm. It appears to volatilise with vapour of water. It dissolves without alteration in boiling dilute sulphuric acid, in strong acetic acid, in caustic alkalis. According to Brandes, it forms a peculiar compound with nitric acid. (Gerh. iv. 280.)

CASTOR OIL. This oil, much used in medicine as a purgative, is extracted from the seed of *Ricinus communis*, a euphorbiaceous plant cultivated in the West Indies and other warm climates. It is viscid, yellowish, odourless, and has a faint taste, which becomes acrid when the oil is rancid. It solidifies at − 18° C. Specific gravity 0·969 at 12° C. It is distinguished from other oils by its easy solubility in alcohol and ether. It is a mixture of several glycerides. When saponified by an alkali, it yields a soap perfectly soluble in water, and from which mineral acids separate a mixture of acids, oily at common temperatures, and consisting mainly of ricinoleic acid, $C^{18}H^{34}O^3$. When this oily mixture is dissolved in a third of its volume of alcohol, and the solution is cooled to − 15° or − 12° C., it deposits a small quantity of nacreous scales, apparently consisting of stearic and palmitic acids.

Castor-oil gives by analysis:

	Saussure.	Ure.	Lefort.	
Carbon . . .	74·18	74·00	74·58	74·35
Hydrogen . .	11·03	10·29	11·48	11·35
Oxygen . . .	14·79	15·71	13·94	14·30
	100·00	100·00	100·00	100·00

Ammonia converts castor-oil into ricinolamide, $N.H^2.C^{18}H^{33}O^2$. When castor oil is distilled with potash, sebate of potassium remains in the retort, and an oily liquid passes over, consisting of caprylic or œnanthylic alcohol, and methyl-œnanthyl (see ALCOHOLS, p. 98). Castor-oil treated with a mixture of sulphuric acid and acid chromate of potassium, yields œnanthylic acid and hydride of valeryl. Nitric acid attacks it with violence, and converts it into œnanthylic acid. Peroxide of nitrogen causes it to solidify. Castor-oil dissolved in absolute alcohol, and exposed to the action of gaseous hydrochloric acid, is converted into glycerin, and contains ethyl-compounds formed by the fatty acids previously in combination with the glycerin. Castor-oil subjected to dry distillation, yields hydride of œnanthyl and œnanthylic acid, together with small quantities of acrolein and solid fatty acids. (Gerh. ii. 903.)

CATALYSIS, or *Contact action.*—Terms applied by Berzelius and Mitscherlich to those cases of chemical action in which a substance appears to induce decomposition in another body, without itself undergoing perceptible alteration, or at all events without entering into combination with either of the elements of that compound. (See CONTACT ACTION.)

CATAPLEIITE. A silicate containing zirconium, from the island Lamö, near

Brevig, Norway, together with zircon, leucophane, mosandrite, and tritomite. Imperfect prismatic crystals, with perfect basal cleavage. Specific gravity 2·8. Hardness near 6. Opaque, with light yellowish-brown colour, and little lustre. Melts easily to a white enamel before the blowpipe on platinum; gives a colourless glass with borax; blue with cobalt-solution. Dissolves easily in hydrochloric acid without gelatinising. Mean of analyses:

SiO^2	Zr^4O^3	Al^4O^3	Na^2O	Ca^2O	Fe^2O	H^2O	
46·67	29·57	0·92	10·45	4·13	0·56	8·96	= 101·26

agreeing nearly with the formula $3(M^2O.SiO^2) + 2(Zr^4O^3.3SiO^2) + 2aq.$, which if zirconia be regarded as a protoxide ($zr = \frac{2}{3}Zr$), may be reduced to that of a metasilicate $(M^2zr^4)Si^3O^9 + aq.$ (Weibye and Sjögren, Pogg. Ann. lxxix. 299; Dana, ii. 308.)

CATAWBARITE. A name given by Lieber (Sill. Am. J. xxviii. 148), to a rock which accompanies itacolumite, and appears to stand, as a magnesium rock or slate, between itacolumite and itabirite.

CATECHU, formerly called also *Terra japonica*, is an extract rich in tannin, obtained by boiling in water the parts of several plants growing in India, and is distinguished into three sorts in commerce. 1. Bombay Catechu, from the *Areca catechu*, is prepared by boiling the fruit of the *areca* palm in water, the first portions of the decoction being the strongest, and affording the quality called *Cassu*, the latter portions, the weaker sort called *Coury*. The best occurs in dense irregular lumps of a dark brown colour. It is opaque, with an even, slightly unctuous, shining fracture. Another variety called *catechu verum* has a somewhat reddish-brown colour, a fatty lustre, a splintery conchoïdal fracture, and is translucent on the edges. Bombay catechu is almost entirely soluble in boiling water, yielding a dark brown liquor, very rich in tannic acid, and affording copious precipitates with solution of glue and with sulphuric acid.

2. Bengal Catechu, is obtained from the *Acacia* (*Mimosa*) *Catechu*, by boiling the twigs and unripe pods in water. It has a lower specific gravity, is of a pale brown colour, with a yellowish cast. It is opaque, with a glimmering lustre on the fractured surface only, and traversed by dark brown shining stripes. When treated with cold water, it leaves a large residuum, but boiling by water it is mostly taken up; the solution contains less tannin, but more *catechin*, than the Bombay sort.

3. The third kind, called Gambir Catechu, is referred to the *Nauclea* (*Uncaria*) *Gambir*, from which also kino is obtained. It occurs in cubical pieces of 1 to 1½ inches, opaque, and of a brown yellow or bright yellow colour. Their fracture is even and dull. It is little soluble in cold water, but almost completely in boiling water, the solution affording copious precipitates with glue and sulphuric acid.

4. A fourth kind called Egyptian or Nubian Catechu, is said by Landerer to be obtained by the collectors of gum by boiling the fruits of gummiferous acacias, and to be exposed for sale in the bazaars of Smyrna, and at Constantinople. It is for the most part soluble in water, but differs from the other varieties in many respects.

All kinds of catechu dissolve in great measure in alcohol; and soften with heat. The specific gravity of good Bombay catechu is 1·39; of Bengal catechu 1·28; and of the Gambir variety, 1·40. Catechu is used as an astringent in medicine, and for tanning leather, either alone or mixed with oak bark. The comparative value of catechu for tanning may be measured by the proportion of gelatin which is required to precipitate all its tannin. Catechu is also used in dyeing, especially for silk and wool. When treated with nitric acid at 45° C., it yields a bright yellow powder, possessing all the properties of picric acid, but much more soluble in water. Silk and wool may be easily dyed in the aqueous solution.

Catechu has lately been much used to prevent the formation of boiler incrustations, or to remove them when formed; the quantity required is such as will slightly colour the water. (Newton, Rep. of Patent Inventions, 1858; Dingl. pol. J. cxlviii. 315.)

Catechu is *mainly* composed of two principles, *catechin* and *catechutannic acid*, together with a brown colouring matter.

CATECHIN, *Catechucic acid*, or *Tanningenic acid*, is obtained from Bengal catechu, by digesting it for 24 hours in cold water to extract the tannin, and then boiling the residue several times with water. The yellow catechucic acid which deposits itself during the cooling is to be collected upon a filter, washed repeatedly with cold water, and finally dissolved in six times its weight of water with purified bone-black to decolorise it. White catechucic acid separates from the hot filtered solution as it cools. It is now to be washed on a filter with cold water, quickly dried on bibulous paper, and more completely under the receiver of the air-pump. Other processes, but less simple, have been prescribed.

Pure catechin is a white powder composed of very small silky needles. It dissolves in 1133 pts. of water at 17° C., forming a colourless tasteless solution, which has no effect on the colour of litmus; it dissolves in 3 pts. of boiling water (forming a solution said to have an acid reaction), in 5 or 6 pts. of cold alcohol, 2 or 3 pts. boiling alcohol 120 pts. of cold ether and 7 to 8 pts. boiling ether. According to Zwenger's analysis it contains 61·3 per cent. carbon and 4·8 hydrogen, whence Zwenger deduces the formula $C^{20}H^{18}O^{8}$.

Catechin melts at 217° (Zwenger), and solidifies to a translucent, amorphous, brittle mass. After drying at 100° C. it gives off 4·4 per cent water when melted. When heated above its melting point, it turns brown, and intumesces, giving off water and carbonic acid. By dry distillation it yields an empyreumatic oil and an acid watery liquid, which yields by evaporation crystals of pyrocatechin or oxyphenic acid (*q. v.*)

Dilute mineral acids dissolve catechin without altering it; strong acids decompose it; with strong sulphuric acid it forms a deep purple liquid.

Catechin does not form definite compounds with bases. It absorbs ammonia, but gives it up again in vacuo. The fixed alkalis colour it yellow, brown, and black. It does not decompose alkaline carbonates, or precipitate the solutions of hydrate or acetate of calcium or barium. It forms a white precipitate with acetate and subacetate of lead; dark green with ferric chloride; greenish-black or violet with ferroso-ferric sulphate; brown or black with sulphate of copper; brown or black with salts of silver, gold, and platinum, the metals being reduced. These decompositions often take place after a time only, or on heating the liquid, and are always accompanied by decomposition of the catechin. Solutions of gelatin, starch, tartar-emetic, and salts of quinine or morphine, are not precipitated by catechin. (Gerh. ii. 882).

CATECHU-TANNIC ACID. *Cachoutannic acid. Tannin of Catechu.* To obtain this acid, the aqueous infusion of catechu is heated with dilute sulphuric acid, and after the liquid has been clarified from the colouring matter, &c., thereby thrown down, strong sulphuric acid is added as long as a precipitate continues to form. This precipitate is washed on a filter with dilute sulphuric acid, pressed between paper, and dissolved in pure water, the solution digested with carbonate of lead, the solid matter thrown on a filter, and the filtrate evaporated in vacuo. The product thus obtained is purified by re-solution in ether containing alcohol. Another mode of preparation is to exhaust powdered catechu with ether in a displacement-apparatus and evaporate the ethereal solution. A yellowish porous mass then remains resembling gallotannic acid.

Cachoutannic acid has a purely astringent taste, and resembles gallotanic acid in many of its properties, but is distinguished therefrom by not precipitating tartar-emetic, and by forming a greyish-green precipitate with ferric salts. It does not precipitate ferrous salts. It is soluble in water, alcohol, or ether, insoluble in oils both fixed and volatile; its solutions are precipitated by gelatin. It is but slightly soluble in water acidulated with sulphuric acid, though more so than gallotannic acid.

According to Pelouze, catechutannic acid contains $C^{18}H^{18}O^{8}$.

Catechutannic acid softens when heated, and yields by distillation a yellow empyreumatic oil, together with a watery liquid which gives a greenish-grey precipitate with ferric salts, and is coloured brown by alkalis.

The solution of catechu-tannic acid alters quickly by exposure to the air, becoming red, and leaving on evaporation a substance which no longer re-dissolves completely in water. According to Delffs, catechin is one of the products of the decomposition.

The salts of catechutanuic acid are too unstable to be prepared in the pure state. The *potassium-salt* is very soluble, and precipitates gelatin after addition of an acid. The catechutannates of the earth-metals and heavy metals form sparingly soluble precipitates.

CATHA EDULIS. The leaves of this plant, called *Kât* by the Arabs, are brought from the interior to Aden; they are said to produce sleeplessness and an agreeable state of excitement.

CATHARTIN. The purgative principle of senna (the leaves and fruits of several shrubs of the genus *Cassia*, order *Leguminosæ*). It is prepared by evaporating the alcoholic extract of senna, redissolving in water, precipitating with acetate of lead, separating the excess of lead from the solution by sulphuretted hydrogen, and evaporating the filtrate. It is a brownish yellow, uncrystallisable, diaphanous mass, soluble in water and alcohol, insoluble in ether; its taste is bitter and disgusting. By dry distillation it yields products free from nitrogen. Alkalis turn it brown; with subacetate of lead and tincture of galls, it forms yellow precipitates (Lassaigne and Feneuille, Ann. Ch. Phys. [2] xvi. 18). Winckler (Jahrb. pr. Pharm. xix. 223) applies the term *cathartin* to a bitter substance contained in the berries of the buckthorn (*Rhamnus catharticus*). (See RHAMNO-CATHARTIN.)

CATHODE, or *Kathode.*—Faraday's term for the negative pole or electrode in the voltaic circuit, the elements there eliminated being called *cations*, or *kations*. (See ANION, p. 296.)

CATLINITE. A reddish clay stone from the Coteau de Prairies, west of the Mississippi. (Jackson, Sill. Am. J. xxxv. 388.)

CAT'S EYE. A translucent quartz of beautiful appearance brought from Ceylon. Its colours are green, grey, brown, and red of various shades. Fracture imperfectly conchoïdal. Translucent with vitreous internal lustre. It derives its name from a peculiar play of light (*chatoyant*), arising from fibres interspersed. It scratches quartz, is easily broken, and resists the blowpipe. Specific gravity 2·64. Contains, according to Klaproth, 95 per cent. silica, 1·75 alumina, 1·5 lime, and 0·25 oxide of iron. It is valued for setting as a precious stone. U.

CAULOPHYLLIN. A resinous medicinal preparation obtained in North America from *Caulophyllum Halictroïdes.* (Buchner's N. Repert. vi. 188.)

CAUSTICITY. The quality possessed by strong alkalis, acids, nitrate of silver, &c., of corroding the skin and flesh of animals. In the old language of surgery, caustics were divided into the actual, such as red-hot iron and *moxa*, and the potential, such as the above-mentioned preparations.

CAVOLINITE. See Nephelin.

CAWK. A miner's term for native sulphate of barium.

CEDAR, OIL OF (not to be confounded with *Oleum de cedro*, which is one of the names of oil of citron).—A volatile oil obtained from the wood of the Virginian cedar, *Juniperus Virginiana*, which is used for making pencils, and owes its agreeable odour to this oil. It is a soft semi-solid mass, consisting of a liquid hydrocarbon, cedrene, $C^{15}H^{24}$, and an oxygenated camphor or stearoptene, containing $C^{15}H^{26}O$.

To obtain the camphor, the crude oil is distilled; the distillate is pressed between linen or calico, to free it from the greater portion of the liquid cedrene which adheres to it, and then crystallised from alcohol of ordinary strength, which retains the rest of the cedrene in solution.

Cedar-camphor thus purified is a crystalline mass of great beauty and lustre, having an aromatic odour, like that of pencil-wood, but not much taste. It melts at 74° C. and boils at 282°. Vapour-density = 8·4. It dissolves very sparingly in water, but freely in alcohol, whence it crystallises in needles having a silky lustre. It gives by analysis, 81 per cent. carbon and 11·8 hydrogen, agreeing with the preceding formula; hence it is isomeric with camphor of cubebs (*q. v.*) By distillation with phosphoric anhydride, it is resolved into water and cedrene, $C^{15}H^{26}O = C^{15}H^{24} + H^2O$. With pentachloride of phosphorus, it yields an aromatic substance, which has not yet been analysed. Strong sulphuric acid colours it strongly and separates an amber-coloured oil (Walter, Ann. Ch. Phys. [3] I. 1. 498). According to Bertagnini (Compt. rend. xxxv. 800), oil of cedar combines wth the acid sulphites of the alkali-metals.

CEDRENE. $C^{16}H^{24}$.—This body is produced from the concrete portion of cedar-oil by the action of phosphoric anhydride. It is oily, aromatic, and has a peppery taste. Specific gravity 0·984 at 15° C. Boils at 248°. Vapour-density 7·5 (4 vol.) (Walter, *loc. cit.*)

CEDRIN. See Cedron.

CEDRIRET. One of the products obtained by Reichenbach (J. pr. Chem. i. 1) from the tar of beech-wood; said to crystallise in fine needles. Völckel (Ann. Ch. Pharm. lxxxvi. 331) was not able to find it.

CEDRON. *Simaba Cedron* (Planchon).—A tree which grows in the hottest parts of New Granada, and bears fruits resembling the bean of St. Ignatius; they have a bitter taste, and are used in that country as medicine. Ether extracts from them a neutral crystallisable fat, insoluble in cold alcohol. The fruit, after exhaustion with ether, yields to alcohol a crystallisable substance, cedrin, which Lewy regards as the active principle of the fruit. Cedrin is sparingly soluble in cold water, more soluble in boiling water and in alcohol, and crystallises from the solutions in silky needles. It is neutral, and has an intensely and persistently bitter taste. (Lewy, Compt. rend. xxxii. 510.)

CELESTIN. Syn. with Cœlestin.

CELLULIC ACID. Syn. with Metapectic Acid. (See Pectic Acid.)

CELLULOSE. $C^6H^{10}O^5$. *Lignin, Woody fibre. Ligneux. Zellstoff, Planzenzellstoff, Pflanzenfaserstoff.* (Payen, *Précis de Chimie industrielle*, 4^{me} éd. ii. 11; Gerh. ii. 481; Gm. xv. 123.)—This substance constitutes the essential part of the solid framework of plants. The cell-walls in the early stages of their development are composed entirely of it, but as the plant grows, they become incrusted with colouring matter, resins, and other foreign substances, which in some parts, as in the heart-wood of large trees, fill up the entire cavities. Some tissues, however, consist almost wholly of cellulose, *e. g.* the pith of the rice-paper plant (*Aeschynomene paludosa*), and the horny perisperms of certain seeds, as those of the phytelephas or vegetable ivory, the date-tree, dragon-tree, &c. Several manufactured vegetable fabrics, as cotton, linen, hemp, and unsized white paper, consist of cellulose very nearly pure.

Cellulose has also been said to exist in the animal kingdom, constituting the chief part of the mantle of mollusca, and according to Frémy, of the testa or integument of insects and crustacea; from the analysis of other chemists, however, these substances appear to be nitrogenous (see CHITIN). According to Virchow (Compt. rend. xxxvi. 492, 860), cellulose is found in degenerated human spleen and in certain parts of the brain.

The easiest method of obtaining pure cellulose, is to wash white cotton, unsized paper, old linen, or elder-pith, with a hot solution of caustic potash or soda, then with cold dilute hydrochloric acid, then with ammonia, washing thoroughly with water after the application of each of these reagents, and lastly with alcohol and ether; it is often necessary to repeat this series of operations two or three times. To obtain pure cellulose from wood, it is necessary, after boiling the wood with potash till the liquid is almost dry, to treat it with chlorine-water or with a weak solution of chloride of lime, repeating these successive operations several times, in order to free the cellular tissue from the encrusting matter which is so intimately united with it. The vegetable fibres in the excrements of herbivorous animals furnish a convenient source of cellulose, because the encrusting matter has been already removed or disintegrated to a great extent by the process of digestion, so that the cellular substance which remains is much easier to purify than the tissue of the plant in its natural state.

Cellulose thus purified is white, translucent, of specific gravity about 1·5, insoluble in water, alcohol, ether, and oils, both fixed and volatile. When quite pure, it is unalterable in the air; but as it exists in wood, in contact with azotised and other easily alterable matters, it gradually decomposes in moist air, undergoing a slow combustion, and being converted into a yellow or brown friable substance called *touchwood*.

The state of aggregation of cellulose varies with its origin. In its less compact forms, as in Iceland moss, it is easily disintegrated by boiling with *water*, and converted into a soluble substance, viz. dextrin; but in its ordinary denser form, as in wood, linen, cotton, &c. it resists the action of water, and even of more energetic solvents, for a long time.

Strong *sulphuric* and *phosphoric acid* disintegrate cellulose at ordinary temperatures, and convert it into dextrin, a substance isomeric with cellulose, without colouring it; if water be then added and the mixture boiled, the dextrin is converted into glucose. Thin strips of paper or linen, triturated with strong sulphuric acid added drop by drop, are converted, after some time, into a viscous mass consisting of dextrin, and on boiling this mass with water, it acquires the property of reducing copper-salts in presence of an alkali, and after some hours' boiling is completely converted into glucose.

Unsized paper plunged for a few seconds into sulphuric acid diluted with half to a quarter its bulk of water, and then washed with weak ammonia, undergoes a very remarkable alteration, being converted, without change of composition, into a tough substance very much resembling animal parchment, and applicable to the same purposes. The formation of this remarkable substance was first noticed in 1847, by Messrs. Poumarède and Figuier, who gave to it the name of *Papyrin*. The discovery remained, however, without practical application till the year 1857, when it was again brought into notice and patented in this country by Mr. W. E. Gaine; and the material, called *vegetable parchment*, or *parchment paper*, is now manufactured in large quantity by Messrs. De la Rue and Co. Besides its application to the same purposes as ordinary parchment, it is largely used for covering pots in which preserves and jellies are kept, and for making shirt-collars, imitation lace, &c. &c.; it is also very useful in the laboratory, for connecting pieces of apparatus in distillations, and as an intervening membrane in experiments of diffusion, osmose, &c. That it should have remained so long unnoticed after its first discovery is probably due to the circumstance that Messrs. Poumarède and Figuier, in preparing it, used strong sulphuric acid, of specific gravity 1·842; and it has since been found that the material thus produced, though possessing the general characters above described, is not nearly so tenacious as that obtained with acid diluted to the extent already mentioned. (Hofmann, Ann. Ch. Pharm. cxii. 243.)

Cellulose (linen, for example), boiled for a short time with *moderately dilute sulphuric* or *nitric* acid, is converted into a pulpy mass, which still exhibits the composition of cellulose, and does not dissolve sensibly in water. *Strong boiling hydrochloric acid* converts cellulose into a fine powder, without change of composition. *Moderately strong nitric acid* converts cellulose into a nitro-substitution-product, resembling xyloïdin, $C^6H^9(NO^2)O^5$ (*q. v.*) With *very strong nitric acid*, or a mixture of strong *nitric* and *sulphuric acids*, higher substitution-products are formed, viz. $C^6H^8(NO^2)^2O^5$ and $C^6H^7(NO^2)^3O^5$ called gun-cotton, or pyroxylin (*q. v.*)

Caustic potash or *soda* disintegrates cellulose but slowly, and with the more compact varieties the effect is merely superficial. When equal parts of potash and cellulose, moistened with water, are heated in a closed vessel, hydrogen is evolved, and wood-spirit distils over, while formic, acetic, and carbonic acids are produced, and remain with the alkali. Melted hydrate of potassium converts cellulose into malic acid.

Cellulose in all its forms is immediately blackened by *fluoride of boron.*

When *chlorine gas* is passed into water in which cellulose is suspended, the cellulose is rapidly oxidised, with evolution of carbonic acid; the same effect is produced on gently heating cellulose with the solution of a *hypochlorite:* hence in bleaching cotton or linen fabrics, paper-pulp, with hypochlorites, &c., great care must be taken not to use too strong a solution.

Cellulose in its more compact forms is not coloured by solution of *iodine;* but if previously disintegrated by sulphuric acid or caustic alkalis, it produces a violet-blue colour with iodine. In this manner, cellulose may be detected in vegetable tissues under the microscope. Some lichens and algæ, Iceland moss for example, give the blue colour with iodine after being boiled with water.

Solution of Cellulose.—Cellulose dissolves completely in an *ammoniacal solution of oxide of copper.* This solvent may be prepared by passing air freed from carbonic acid into a bottle filled with copper turnings and half filled with ammonia; or by placing copper turnings which have been oxidised on the surface by heating them in the air and then reduced by dry hydrogen, in a tall glass vessel, and causing ammonia to drop through them into a bottle placed below; or again, by directly dissolving oxide of copper in ammonia. Silver-paper, or thin filtering-paper, dissolves in this liquid after a while, forming a syrupy solution, which may be filtered after dilution with an equal bulk of water. On mixing the liquid thus formed with excess of hydrochloric acid, the cellulose is precipitated in amorphous flakes, which, after washing with water, are colourless and quite free from copper. Even in this finely divided state, cellulose is not coloured blue by iodine, unless it be first subjected to the action of strong sulphuric acid. (Payen.)

Several substances obtained from the solid tissue of plants, and formerly regarded as distinct proximate principles, are now known to be mere modifications of cellulose; *e. g. fungin*, from fungi, *medullin*, from the pith of various trees, &c. *Hordein*, from barley, is a mixture of cellulose with starch and a nitrogenous body.

CELTIS. The fruit of *Celtis orientalis* contains 71 per cent. of fleshy pericarp, and 28·3 seeds, the latter consisting of 67·3 husks, and 32·7 kernel; 100 pts. of the kernels contain 15·2 pts. oil, and 45·6 ash, of which 40·4 pts. consist of carbonate of calcium, and 4·4 of silica.

CEMENT. The term cement is applied to any substance capable of holding together the surfaces of two bodies without mechanical rivets. Cements may be divided into two classes, stony cements, and those of a resinous and glutinous character.

1. The chief stony cements are *common building mortar*, a mixture of lime slaked to a creamy consistence, and sharp sand, which hardens partly by drying, partly by absorption of carbonic acid from the air; and *hydraulic mortar*, or *Roman Cement*, a mixture of slaked lime with *amorphous silica*, which hardens under water to a compact mass of hydrated silicate of calcium. (See Silicates of Calcium.)

The *mastic cement* of London, much employed for giving to brickwork the hardness and appearance of stone, is composed of oolitic limestone, chiefly that of Portland, finely ground, mixed with sand and litharge, and made into a loosely coherent paste with linseed oil, either raw or boiled. The oil is extemporaneously mixed by the workman with the cement powder on a board by a trowel, and plastered thinly and smoothly over bricks, laths, or any surfaces which are to resemble stones. The fine dust produced by sawing stone slabs, is said to answer a like purpose, when mixed with litharge and oil. Analysis shows that the said *mastic* is composed of 35 pts. of siliceous sand, 62 of limestone, and 3 of litharge. These proportions may, however, be somewhat varied without injury. Too much limestone impairs the hardness of the cement; too much sand makes it porous. For every 100 pts. of such a mixture, about 7 of oil are required. As this compost is friable, it may be made more ductile by keeping it compressed in moulds, for a little time before spreading it by the trowel. The surface to which it is to be applied, must be cleaned and oiled beforehand with a brush. It is particularly useful in closing fissures in buildings, and preventing the ingress of moisture through seams.

2. *Resinous* and *glutinous* cements are of many different compositions. Rosin and beeswax melted together, and thickened with more or less fine brickdust, serve for cementing glass and metal works. Asphalt mixed with chalk in due proportion has been used extensively for paving streets and terraces. The bitumen of Seyssel and Lobsann in France, has been largely employed for this purpose. The compost rendered nearly fluid by heat, is applied to bodies dried, and if convenient, previously heated.

Coal tar mixed with sand, forms a bad composition, which becomes friable and porous by exposure to weather.

Seven or eight parts of rosin, and one of wax, melted together and mixed with a small quantity of plaster of Paris, form a very good cement to unite pieces of Derbyshire spar, or other stone. The stone should be made hot enough to melt the cement, and the pieces should be pressed together as closely as possible, so as to leave as little as may be of the cement between them: this is a general rule in cementing, as the thinner the stratum of cement interposed, the firmer it will hold. Melted sulphur used in the same way will answer sufficiently well, if the joining be not required to be very strong.

It sometimes happens, that jewellers, in setting precious stones, break off pieces by accident: in this case they join them, so that it cannot be easily seen, with gum-mastic, the stones being previously made hot enough to melt it. By the same medium, cameos of white enamel or coloured glass are often joined to a real stone as a ground, to produce the appearance of an onyx. Mastic is likewise used to cement false backs or doublets to stones to alter their hue.

The jewellers in Turkey, who are generally Armenians, ornament watch-cases and other trinkets with gems by glueing them on. The stone is set in silver or gold, and the back of the setting made flat to correspond with the part to which it is to be applied. It is then fixed on with the following cement: Isinglass, soaked in water till it swells up and becomes soft, is dissolved in French brandy, or in rum, so as to form a strong glue. Two small bits of gum galbanum, or gum ammoniacum, are dissolved in two ounces of this by trituration; and five or six bits of mastic, as big as pease, being dissolved in as much alcohol as will render them fluid, are to be mixed with this by means of a gentle heat. The cement is to be kept in a phial closely stopped; and when used, it is to be liquefied by immersing the phial in hot water. This cement resists moisture.

A solution of shellac in alcohol, added to a solution of isinglass in proof spirit, makes another cement that will resist moisture.

So does common glue melted without water, with half its weight of rosin, with the addition of a little red ochre to give it a body. This is particularly useful for cementing hones to their frames.

Clay and oxide of iron mixed with oil, are said to form a cement that will harden under water.

A strong cement, insoluble in water, may be made from cheese. The cheese should be that of skimmed milk, cut into slices, throwing away the rind, and boiled till it becomes a strong glue, which, however, does not dissolve in the water. This water being poured off, it is to be washed in cold water, and then kneaded in warm water. This process is to be repeated several times. The glue is then to be put warm on a levigating stone, and kneaded with quick lime. This cement may be used cold, but it is better to warm it; it will join marble, stone, or earthenware, so that the joining is scarcely to be discovered.

Boiled linseed oil, litharge, red lead, and white lead, mixed together to a proper consistence, and applied on each side of a piece of flannel, or even linen or paper, and put between two pieces of metal before they are brought home, or close together, will make a close and durable joint, that will resist boiling water, or even a considerable pressure of steam. The proportions of the ingredients are not material; but the more the red lead predominates, the sooner the cement will dry, and the more the white, the contrary. This cement answers well for joining stones of large dimensions.

The following is an excellent cement for iron, as in time it unites with the metal into one mass:—Take two ounces of sal-ammoniac, one of flour of sulphur, and sixteen of cast-iron filings or borings. Mix them well in a mortar, and keep the powder dry. When the cement is wanted for use, take one part of this mixture, twenty parts of clear iron borings or filings, grind them together in a mortar, mix them with water to a proper consistence, and apply them between the joints.

Powdered quick lime mixed with bullock's blood, is often used by coppersmiths to lay over the rivets and edges of sheets of copper in large boilers, as a security to the junctures, and also to prevent cocks from leaking.

Six parts of clay, one of iron filings, and linseed oil sufficient to form a thick paste, make a good cement for stopping cracks in iron boilers.

Temporary cements are wanted in cutting, grinding, or polishing optical glasses, stones, and various small articles of jewellery, which it is necessary to fix on blocks, or handles, for the purpose. Four ounces of rosin, a quarter of an ounce of wax, and four ounces of whiting made previously red-hot, form a good cement of this kind, as any of the above articles may be fastened to it by heating them, and removed at pleasure in the same manner, though they adhere very firmly to it when cold. Pitch, rosin, and a small quantity of tallow, thickened with brick-dust, is much used at Birmingham for these purposes. Four parts of rosin, one of beeswax, and one of brickdust, likewise make a good cement, which answers extremely well for fixing knives and forks in their hafts; but the manufacturers of cheap articles of this kind too commonly use rosin and brickdust alone. On some occasions, in which a very tough cement is requisite, which will not crack though exposed to repeated blows, as in fastening to a block metallic articles that are to be cut with a hammer and punch, workmen usually mix some tow with the cement, the fibres of which hold its parts together.

Excellent water-proof cements are made from caoutchouc (p. 739).

The following composition is a good cement for electrical apparatus:—Five pounds of rosin, one of beeswax, one of red ochre, and two table spoonfuls of plaster of Paris, all melted together. A cheaper one for cementing voltaic plates into wooden troughs is made with six pounds of rosin, one pound of red ochre, half a pound of plaster of Paris, and a quarter of a pint of linseed oil. The ochre and plaster of Paris should be well dried, and added to the other ingredients in a melted state.—U. (See *Ure's Dictionary of Arts, Manufactures and Mines*, i. 641).

CEMENTATION is the process by which one solid is made to penetrate and combine with another at a high temperature so as to change the properties of one of them, without liquefaction taking place, being an exception to the general chemical rule, that bodies do not mutually act on each other unless when one or more of them is fluid. The conversion of iron into steel by absorption of carbon into its inmost substance, from a mass of ground charcoal in which it lies embedded while exposed to strong ignition, is one of the best examples of this process. A like change takes place on palladium, iridium, and platinum, in contact with charcoal or silica at a high heat. When a compact mass of the oxide of nickel or iron is ignited in a crucible lined and covered with charcoal, the carbon exerts its deoxidating and metallising power to the very centre. The same phenomenon occurs with compact sulphate of potassium or sodium encased and heated to redness in charcoal, these salts being thereby converted into metallic sulphides. These transformations have been ascribed to the progressive production of the gaseous oxide of carbon, and to its absorption by the metals, or its combination with the oxygen of the oxides or acids. U.

CEMENT COPPER, is the metal precipitated from the blue water of copper mines or works by plunging iron plates into them. (See COPPER.)

CENTAURIN. See CNICIN.

CENTRALLASSITE. A hydrated silicate of calcium occurring in kidney-shaped lumps, together with other minerals, at Fundy Bay. These lumps are coated with a greenish crust resembling chlorite; below this crust is a thin layer of cerinite; within this the centrallassite; and the central portion consists of cyanolite. Centrallassite exhibits a lamellated radiating structure; it is white or yellowish, translucent, brittle, of specific gravity 2·45 to 2·46, hardness 3·5, and has an almost waxy lustre. It melts before the blowpipe with intumescence to an opaque glass, and forms clear beads with fluxes. It dissolves in hydrochloric acid without gelatinising. Its analysis is said to agree with the formula $8Ca^2O.15SiO^2 + 5aq$. (H. How, Edinb. N. Phil. J. x. 847.)

CEPHALIS. See IPECACUANHA.

CEPHALOTE. *Ceranocephalote.*—A name applied by Couerbe (J. Chim. Med. x. 524) to a yellow elastic fatty substance, insoluble in alcohol, but soluble in ether, which he obtained from the brain. According to Frémy and J. R. Simon, it is a mixture of the cerebrates of potassium and sodium, with traces of olein and oleophosphoric acid.

CERADIA FUSCATA. A plant indigenous on the coast of Africa, which exudes an amber-brown resin smelling like olibanum.

CERAIC ACID. An acid containing $C^{20}H^{40}O^3$, said by Hess (Ann. Ch. Pharm. xxvii. 3) to be formed by oxidation in beeswax; also supposed to be produced in the preparation of oxalic or saccharic acid by the action of nitric acid on wheat-starch; existing also, according to Oppermann (Ann. Ch. Phys. [2] xlix. 240), in a Brazilian wax. Its existence has not been distinctly proved.

CERAIN. A name applied by Boudet and Boissenot (J. Pharm. xiii. 38) to the portion of beeswax which is sparingly soluble in alcohol, and, according to their statement, is not saponified by potash. It appears to be chiefly impure myricin, inasmuch as that body is not quite insoluble in alcohol.

CERANCEPHALOTE. See CEPHALOTE.

CERANTIC ACID. An acid found by Braconnot (Ann. Ch. Phys. [3] xxi. 484) in the fuel taken out of an antique lamp, probably of the fourth century. This material was partly soluble in boiling alcohol of 36°. The solution on cooling deposited a white flaky substance melting at 64° C., probably *cerin:* and the alcoholic mother-liquor retained a substance, which remained after evaporation, as a white, hard, brittle mass, melting at 51° C.; its alcoholic solution reddened litmus, and by slow evaporation deposited small granular crystals. This more soluble substance Braconnot designated *cerantic acid.* The portion insoluble in boiling alcohol contained myricin.

CERASIN. The gum which exudes from the cherry-tree, plum-tree, and others of the same family is only partly soluble in water. The soluble portion exhibits the characters of arabin; the remaining portion, which is called *cerasin*, merely swells up in water. Cerasin is colourless, semi-transparent, tasteless, and inodorous; easily pulverised, uncrystallisable, insoluble in water and in alcohol, not susceptible of alcoholic fermentation. Treated with nitric acid, it yields 15·5 p. c. mucic acid. According to Gélis (Compt. rend. xliv. 144) ordinary gum arabic is converted into insoluble cerasin by a heat of 150° C. This artificial cerasin is reconverted into a soluble gum by prolonged boiling with water, but again becomes insoluble when heated to 150°.

CERASINE or **CERASITE.** Syn. with Horn Lead.

CERASUS. The wood of *Cerasus avium*, the bird-cherry, contains 0·28 per cent., the bark 10·37 per cent. of ash. The constituents of these ashes are as follows:

	K^2O	Na^2O	Ca^2O	Mg^2O	Fe^4O^3	P^2O^5	SO^3	SiO^2	Cl
Wood . .	25·9	10·4	35·8	11·4	0·1	9·6	4·1	2·5	trace
Bark . .	7·9	15·5	44·7	5·4	0·2	3·5	0·8	21·3	0·4

The unripe fruit of *C. caproniana* contains a large quantity of malic acid.

C. capricida is known in Naples, and *C. virginiana* in North America, as deleterious.

CERATE. A mixture of wax with oil or lard, used by surgeons to screen ulcerated surfaces from the air. Sometimes watery liquids are incorporated with the mass, as subacetate of lead in lead-cerate. U.

CERAUNITE. Syn. with Nephrite.

CEREALIN. A nitrogenous substance closely resembling diastase, obtained by Mège-Mouriès (Compt. rend. xxxvii. 351; xxxviii. 505; xlii. 1122; xlviii. 431; l. 467) from bran. It is contained in the epispermium, the sixth membrane of the seed, reckoning from without, and possesses the power of converting starch into dextrin, sugar, and lactic acid. The brown colour of bread made with flour containing bran appears to be chiefly due to the decomposition of a portion of the flour by the cerealin of the bran (see Bread, pp. 658, 660). Stiff starch-paste is quickly converted into a thin liquid by an infusion of bran at 40° or 50° C.

To isolate cerealin, bran is treated for six hours with dilute alcohol, the residue pressed, and this treatment repeated three times, whereby the bran is freed from sugar and dextrin, while the cerealin remains unaltered and undissolved. On treating the residue with water, the cerealin is dissolved, and the aqueous solution evaporated at 40° C. leaves it in the form of an amorphous albuminoïd substance easily soluble in water, insoluble in alcohol, ether, and oils. The solution coagulates at 75° C., also on addition of alcohol; it is precipitated in flakes by dilute acids, not altered by neutral rennet. Its peculiar action on starch is prevented by the presence of alkalis. Cerealin once coagulated is no longer soluble in acids or alkalis, but still possesses the power of transforming starch, though slowly. Cerealin retains its power of decomposing starch at 70° C., but not at higher temperatures, whereas diastase does not lose this power below 90° C. In other respects the two bodies appear to resemble each other exactly.

According to recent investigation by Mouriès, bran freed from cerealin, especially the *perispermium*, appears to be more active than cerealin itself, and possesses the power of converting starch even at 100° C.

CEREALS. *Cerealia. Getreide.*—This name is applied to the grasses which are cultivated for human food, viz. wheat, barley, rye, oats, maize, and rice. They are for the most part distinguished by the large quantities of starch, nitrogenous compounds, and phosphoric acid contained in their seeds, which constituents it is the object of cultivation to develop as much as possible. The several kinds of cereal grain, excepting rice, contain nearly the same amount of nitrogen; but in wheat-grain, the nitrogenous matter (gluten) possesses a peculiar adhesiveness, arising from the presence of a glutinous substance called *gliadin*, which is wanting in the other cereals. It is this property which renders wheat-flour so peculiarly adapted for the making of bread (p. 657).

From the numerous analyses that have been made of the grain and straw of these plants, we select the following:

Way and Ogston have determined the amount of water and ash in the grain, straw, and chaff of wheat barley, oats, and rye with the following results (Journal of the Royal Agricultural Society, vii. [2] 593—678; Jahresber. f. Chem. 1849, p. 672):

Species and Varieties.	Moisture in 100 pts. of			Specific Gravity of the Grain.	Weight of 1 bushel in lbs.	Ash in 100 pts. of dry			Weight of Straw | Chaff. that of the Grain = 1000.	
	Grain.	Straw.	Chaff.			Grain.	Straw.	Chaff.	Straw	Chaff
WHEAT:										
Hopeton . . .	12·00	13·70	12·00	1·374	60	2·00	4·40	10·43	1107	204
,, . . .	12·00	12·30	12·00	1·342	59	2·06	4·30	10·56	987	206
,, . . .	11·00	12·20	11·00	1·354	61	1·69	4·46	12·74	1163	194
,, . . .	9·50	—	—	1·412	60	1·72				
,, . . .	11·50	—	—	1·356	56	1·84				
,, . . .	11·50	14·30	13·50	1·403	63	1·81	4·77	14·39	927	148
,, . . .	12·00	13·30	13·00	1·382	61·5	1·81	4·93	16·42	1009	156
,, . . .	12·00	11·80	13·00	1·396	62	1·94	4·61	13·55	1066	154
,, . . .	12·00	12·00	11·00	1·393	60	1·92	5·85	13·64	1246	175
,, . . .	12·50	13·70	11·50	1·391	63	2·01	4·82	11·70	1167	185
,, . . .	13·00	—	—	1·371	—	1·70				
April . . .	11·00	10·80	12·50	1·357	61	2·01	4·18	7·93	997	278
Spring . . .	12·00	12·44	12·21	1·373	62	1·92	5·79	18·76	1155	175
,, . . .	11·00	12·00	11·00	1·376	58	1·95	5·22	12·99	963	219
,, . . .	13·00	14·00	12·01	1·370	63	1·83	4·65	16·34	1175	165
,, . . .	11·00	11·73	11·00	1·363	62	1·79	6·77	17·12	1068	176
Bristol red . .	11·50	12·13	11·00	1·370	61·7	1·74	4·46	13·16	965	216
Clovers red . .	11·00	11·80	11·00	1·383	61·5	1·74	3·61	8·55	978	298
Red-chaff Dantzic .	12·50	10·40	12·00	1·387	61	1·55	5·43	14·90	1013	185
Pipers thick set .	13·50	12·60	12·50	1·350	61	1·71	5·70	9·73	928	173
,, ,, .	11·50	10·50	12·50	1·339	59	1·95	12·29	17·12	568	194
White-chaff . .	11·50	10·50	12·00	1·313	59	1·74	5·30	11·61	827	155
Spalding . . .	12·00	10·50	11·50	1·377	61	2·05	4·05	8·94	988	233
White . . .	13·50	12·07	13·19	1·308	60	1·94	3·82	14·97	1184	161
,, . . .	13·00	14·00	12·00	1·351	61	1·82	4·65	15·29	1000	178
,, . . .	12·00	11·70	12·00	1·382	60	1·81	7·92	16·31	1122	207
Creeping . . .	11·50	10·52	13·13	1·375	63	1·75	4·83	18·96	958	188
,, . . .	12·50	10·46	12·00	1·394	62	1·96	6·14	17·11	1071	116
,, . . .	13·00	12·13	12·00	1·387	61	2·18	7·77	16·25	1143	199
,, . . .	13·00	10·05	12·00	1·376	62	1·72	4·54	13·60	1032	166
,, . . .	12·00	10·84	13·00	1·367	61·5	1·93	4·18	15·40	981	179
,, . . .	11·50	11·00	11·00	1·365	62	1·95	4·74	17·30	1272	179
,, . . .	11·00	11·93	12·00	1·372	62·7	1·85	5·23	14·83	1279	186
,, . . .	11·00	13·00	11·00	1·394	63	1·92	4·94	18·50	1192	181
Hammonds . .	13·50	11·00	16·00	1·354	60	2·24	5·23	16·32	932	191
Red Britannia . .	12·00	10·94	13·00	1·369	62	2·07	5·79	16·64	730	169
Red	11·50	12·07	13·50	1·352	60	1·98	6·42	15·05	919	243
Red-straw white .	11·25	—	—	1·385	61	1·91				
,, ,, .	12·00	12·70	12·50	1·381	62	1·95	4·85	11·82	1050	178
,, ,, .	12·50	11·80	14·00	1·392	62	1·97	5·30	16·02	1327	203
,, ,, .	11·50	12·43	13·00	1·362	61	1·81	3·12	8·09	852	192
,, ,, .	11·00	12·30	12·00	1·413	63	1·80	4·79	10·73	1123	205
,, ,, .	11·00	13·19	11·50	1·377	63	2·13	8·47	17·94	1313	197
,, ,, .	12·00	11·63	12·30	1·388	62·5	1·96	5·60	11·00	982	180
,, ,, .	12·00	12·50	12·50	1·386	61	1·94	5·79	12·88	1165	240
French . . .	11·00	—	—	1·341	—	1·74				
Egyptian . . .	10·00	—	—	1·340	—	2·19				
Polish . . .	11·00	—	—	1·385	—	1·68				
Marianople . .	10·00	—	—	1·369	—	1·88				
Old red Lammas .	12·50	—	—	1·387	—	2·10				
BARLEY:										
Unknown variety .	12·00	—	—	—	—	2·43				
Chevalier . .	10·00	—	—	1·260	—	2·50				
,, . .	16·00	—	—	1·234	—	2·82				
Moldavian . .	11·00	—	—	1·268	—	2·38				
,, . .	16·00	—	—	—	—	2·75				
Chevalier (awn) .	15·00	—	—	—	—	14·23				
OATS:										
Hopeton . . .	9·50	—	—	—	—	2·50				
Potato . . .	10·50	—	—	1·191	—	2·73				
,, . . .	11·00	—	—	—	—	4·20				
Polish . . .	11·00	—	—	1·182	—	2·97				
,, . . .	13·00	—	—	—	—	3·80				
Unknown . .	12·00	—	—	—	—	3·12				
Oat-chaff . .	15·00	—	—	—	—	9·22			1500	
RYE:										
English . . .	15·00	—	—	—	—	1·60				

In the 50 samples of wheat enumerated in the preceding table:

The moisture in 100 pts. of grain	varies from	9·5	to	13·5;	mean*	11·76
,, ,, ,, straw	,,	10·4	,,	14·0	,,	11·76
,, ,, ,, chaff	,,	11·0	,,	14·0	,,	12·24
Specific gravity of the grain	,,	1·313	,,	1·413	,,	1·374
Weight in lbs. of 1 bushel of grain	,,	58	,,	63	,,	61·8
,, of straw to 1000 pts. of grain	,,	730	,,	1327	,,	1047
,, chaff ,, ,,	,,	116	,,	278	,,	181
Amount of ash in 100 pts. of dry grain	,,	1·68	,,	2·19	,,	1·99
,, ,, ,, straw	,,	3·61	,,	12·29	,,	5·31
,, ,, ,, chaff	,,	7·93	,,	18·76	,,	13·95

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* The mean of the whole, not the mean between the extreme limits.

TABLE II.—*Composition per cent. of* CEREAL GRAINS *according to various Authorities.*

Authorities.	Name of Species and Varieties.	Water.	Starch.	Fat.	Cellulose.	Gum and Sugar.	Nitrogenous Substance.	Nitrogen.	Ash.	P^2O^5.	SiO^2.
	WHEAT:										
Fehling and Faisst.[1]	Winter wheat (Wurtemberg) . .	14·78	81·95		2·84	—	13·24	—	1·97	0·71	0·14
Millon.[2]	22 samples from Lille, Algeria, and Odessa	12·01—17·70	—	1·41—2·14	1·40—2·35	—	9·92—13·81	1·588—2·729			
Polson.[3]	Old American	10·8	62·3	1·2	8·3	3·8	10·9	—	1·6		
	New Scotch	14·8	56·9	1·2	12·4	5·3	7·0	—	1·5		
Poggiale.[4]	Mean of samples not specified . .	14·5	63·3	1·9	4·2	—	14·4	—	1·7		
Mayer.[5]	Summer wheat	13·47	—	—	—	—	—	2·29	2·19	1·185	
	Winter „ (9 samples) . .	10·97—13·83	—	—	—	—	—	2·01—2·32	1·89—2·36	0·935—1·163	
	BARLEY:										
Fehling and Faisst.[1]	5 samples (Wurtemberg) .	13·91—15·60	79·83—81·08		2·58—4·55	—	12·01—15·73	—	2·62—3·04	0·95—1·13	1·51—0·86
	2 „ free from husk „ .	12·97—14·33	78·60—82·92		1·26—1·84	—	13·71—17·46	—	2·10—2·11	0·99—1·09	0·13—0·17
Polson.[3]	New Scotch	12·0	59·7	2·6	11·5	4·2	13·2	—	2·8		
Poggiale.[4]	Mean of samples not specified . .	13·7	74·5	0·2	3·4	—	7·8	—	0·3		
Mayer.[5]	8 samples	10·75—13·94	—	—	—	—	—	1·90—2·20	—	0·930—1·176	
	OATS:										
Fehling and Faisst.[1]	6 samples (Wurtemberg) .	12·47—14·13	70·24—76·41		10·0—11·39	—	10·69—15·59	—	2·65—3·01	0·66—0·98	0·87—1·33
	2 „ free from husk „ .	14·86—15·06	82·30—82·90		0·92—1·41	—	14·12—14·16	—	2·06—2·13	1·03—1·10	0·14—4·24
Poggiale.[4]	Shelled grain	14·2	61·9	6·1	3·5	—	11·2	—	3·61		
Mayer.[5]	9 samples	11·79—16·40	—	—	—	—	—	1·54—1·92	3·01—3·64	0·801—0·965	
	RYE:										
Fehling and Faisst.[1]	7 samples (Wurtemberg) . . .	12·62—14·70	78·58—85·25		1·24—2·30	—	10·40—15·83	—	1·90—2·30	0·67—0·97	0·11—0·32
Poggiale.[4]	Mean of samples not specified . .	15·5	65·5	2·0	6·4	—	8·8	—	1·8		
Mayer.[5]	Summer rye	14·16	—	—	—	—	—	2·38	—	1·014	
	Winter „ (10 samples) . .	11·77—14·31	—	—	—	—	—	1·91—2·38	—	0·903—1·019	
	MAIZE:										
Polson.[3]	4 samples (American and Russian) .	11·5—13·2	50·1—54·8	4·4—4·7	14·9—20·4	2·3—2·9	8·7—8·9	—	1·6—1·8		
Poggiale.[4]	Mean of samples not specified . .	13·5	64·5	6·7	4·0	—	9·9	—	1·4		
Mayer.[5]	From 5 samples	12·94	—	—	—	—	—	1·74	—	0·913	
	RICE:										
Polson.[4]	Patna (purified)	9·8	78·8	0·1	0·2	1·6	7·2	—	0·9		
Poggiale.[5]	Piedmont	13·7	74·5	0·2	3·4	—	7·8	—	0·3		

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[1] Dingler's Polytechnisches Journal, cxxiv. 223 ; Jahresber. d. Chem. 1852, p. 812. The moisture was determined in the fresh grain ; the other constituents in the grain dried at 100° C.

[2] Compt. rend. xxxviii. 85 ; Jahresber. 1854, p. 791. The amount of dry gluten in the nitrogenous substance varied from 6·0 to 17·04.

[3] Chem. Gaz. 1855, 211 ; Jahresber. 1855, p. 889. The determinations refer to the grain in its ordinary (undried) state.

[4] J. Pharm. [3] xxx. 180, 255 ; Jahresber. 1856, p. 809. The determinations refer to the substance dried at 120° C. ; the water was determined by heating the substance (? fresh or air-dried) to 120° C. The starch includes dextrin.

[5] Ann. Ch. Pharm. ci. 129 ; Jahresber. 1857, p. 637. The water was determined in the air-dried grain ; the other materials in the grain dried at 100° C.

TABLE III.—*Composition per cent. of the* ASH OF CEREAL GRAINS.

Authorities.	Name of Species and Varieties.	Potash, K^2O.	Soda, Na^2O.	Lime, Ca^2O.	Magnesia, Mg^2O.	Ferric Oxide, Fe^4O^3.	Sulphuric Anhydride, SO^3.	Silica, SiO^2.	Carbonic Anhydride, CO^2.	Phosphoric Anhydride, P^2O^5.	Chloride of Potassium.	Chloride of Sodium.	Ash in 100 pts. of fresh Substance.	Ash in 100 pts. of dry Substance.	Sulphur in 100 pts. of dry Substance
	WHEAT:														
Way and Ogston.[1]	Hopeton: 9 samples . .	27·1—36·4	0·1—6·1	1·3—3·2	9·9—14·0	0·1—2·0	trace—1·9	1·4—5·6	0·2	40·0—49·2	—	0·3—1·6	1·5—1·8	1·7—2·05	
	Spalding . .	29·8	5·3	1·9	11·1	0·2	0·1	2·2	0·2	48·2	—	—	1·8	2·05	
	Creeping: 3 samples . .	28·9—31·2	1·3—2·4	1·5—6·8	12·4—13·1	0·1—1·4	0·6—1·6	1·2—5·3	—	45·6—48·5	—	—	1·65—1·73	1·85—1·95	
	Red-straw white: 7 samples . .	26·7—31·1	0·6—3·8	1·15—6·9	9·5—14·2	0·1—3·3	0·1—0·6	2·1—9·7	—	46·6—49·6	—	0·34	1·6—1·7	1·8—2·1	
	Old red Lammas	34·2	4·5	3·2	9·6	2·1	0·3	5·5	—	40·6	—	—	1·8	2·1	
	French . . .	31·4	2·3	3·5	13·9	1·0	0·35	3·05	—	43·5	—	—	1·55	1·7	
	Egyptian . .	36·6	0·5	4·3	11·1	1·2	0·2	5·0	—	41·0	—	—	2·0	2·2	
	Odessa . . .	30·3	1·0	3·2	14·3	0·9	—	4·5	—	45·8	—	—	1·5	1·7	
	Marianople .	35·8	9·1	2·05	14·1	trace	0·2	5·0	—	34·4	—	—	1·7	1·9	
T. J. Herapath.[2]	Grown on irrigated land: 3 samples . .	30·0—31·9	8·9—15·0	0·9—1·4	10·6—12·9	—	0·1—0·2	0·1—0·2	—	46·1—48·7	—	0·3—1·7	1·9	2·3	
	Grown on non-irrigated land: 2 samples . .	33·1—35·4	2·9—3·1	2·2—5·6	9·1—10·1	—	trace	trace	—	48·2—50·0	—	trace	1·9	2·5	
Lawes and Gilbert.[3]	Mean result of 23 samples .	29·35	1·1	3·4	10·7	2·4*	—	2·5†	—	49·7	chlorine 0·13			2·0	
	BARLEY:														
Way and Ogston.[1]	Chevalier: 5 samples . .	20·8—37·2	0·5—1·4	1·5—3·6	2·9—8·7	0·1—2·1	trace—2·7	17·3—32·7	—	25·3—38·8	1·3—5·6	1·0—2·5	2·0—2·3	2·3—2·7	0·7—3·5
	Moldavian: 3 samples . .	19·6—31·6	0·9—4·9	1·2—4·2	8·2—10·2	0·1—1·0	0·3—0·5	24·6—30·4	—	28·7—38·0	—	trace—1·5	1·8—2·3	2·1—2·6	1·4—2·4
	Long-eared Nottingham .	32·0	1·2	3·4	11·0	0·15	trace	21·12	0·5	20·9	—	0·7	2·0	2·20	1·4
	OATS:														
J. P. Norton.[4]	Potato . . .	31·6	—	5·3	8·7	0·9	—	0·9‡	—	49·2	—	0·35	—	2·22	
	Hopeton: 3 samples . .	20·6—21·0	—	6·7—10·1	7·8 11·0	0·4—5·1§	17·4	1·3‖	—	36·5—46·3	1·0—5·3	0·6	—	2·14	

Way and Ogston.[1]	Hopeton: 4 samples . .	13·6—17·8	0·5—3·8	2·8—4·2	6·1—7·3	trace—2·1	1·1—2·5	38·5—51·5	—	18·3—26·5	—	0·9—2·6	2·4—3·6	2·5—3·8	1·8—3·5
	Potato: 4 samples . .	13·1—19·7	0·8—3·0	1·3—3·8	6·5—8·2	0·3—1·3	0·1—1·4	39·8—50·0	—	18·7—29·2	—	0·1	2·7—3·6	2·5—3·3	1·6—2·0
	Polish . . .	24·3	3·8	3·5	7·3	0·7	1·7	41·9	—	14·5	—	0·45	2·65	3·0	
	" . . .	16·3	5·3	8·35	5·9	0·1	4·0	43·2	0·6	16·2	—	—	3·3	3·8	
	Unknown variety . . .	14·0	1·5	4·2	8·8	0·4	0·1	49·4	—	21·5	—	—	2·75	3·1	
	RYE:														
Way and Ogston.[1]	Unknown variety . . .	33·8	0·4	2·6	12·8	1·0	0·2	9·2	—	30·9	—	—	1·4	1·6	
	Unknown variety . . .	16·6	19·9	11·25	13·0	—	0·5	3·6	—	33·5	—	1·6	1·3	2·65	
	Unknown variety . . .	9·4	16·1	15·3	10.1	2·2¶	2·6	14·6	—	25·1	—	4·1	1·0	1·9	
	MAIZE:														
Way and Ogston.[1]	"Forty-day" .	28·4	1·7	0·6	13·6	0·5	trace	1·55	—	53·7	—	trace	1·4	1·5	2·05
Graham, Stenhouse, and Campbell.[3]	Unknown variety . . .	30·7	—	3·1	14·7	0·8	4·1	1·8	—	44·5	Cl 0·5				
	RICE:														
Zedeler.[6]	Carolina . .	20·2	2·5	7·2	4·25	—	—	1·4	—	60·2	—	—	—	0·375	

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[1] Journal of the Royal Agricultural Society, vii. [2] 593—678; xvii. [2] 497; Jahresber. f. Chem. 1849, p. 671 and Table D to p. 656; also 1850, p. 666, and Table A to p. 660.

[2] Journal of the Royal Agricultural Society, xi. [1] 93; Jahresber. 1850, p. 666 and Table A to p. 660.

[3] Chem. Soc. Qu. J. x. 22.

[4] Sill. Am. J. [2] iii. 100, 318; Jahresber. 1847—1848 p. 1089, and Table B to p. 1074.

[5] Chem. Soc. Qu. J. ix. 46; Jahresber. 1856, p. 815.

[6] Ann. Ch. Pharm. lxxiii. 348; Jahresber. 1851, p. 711 and Table C to p. 708.

* Ferric phosphate.

† With sand and charcoal.

‡ And 0·98 sand.

§ With 0·4 to 1·20 Mn^4O^3.

‖ And 2·3 to 4·4 sand.

¶ And 0·5 alumina.

TABLE IV.—*Composition per cent. of the* ASH OF STRAW AND CHAFF OF CEREALS.

Authorities (see p. 827).	Name of Species and Varieties.	Potash, K^2O.	Soda, Na^2O.	Lime, Ca^2O.	Magnesia, Mg^2O.	Ferric Oxide, Fe^4O^3.	Sulphuric Anhydride, SO^3.	Silica, SiO^2.	Carbonic Anhydride, CO^2.	Phosphoric Anhydride, P^2O^5.	Chloride of Potassium.	Chloride of Sodium.	Ash in 100 pts. of fresh Substance.	Ash in 100 pts. of dry Substance.	
	WHEAT:														
Way and Ogston.	Creeping: straw with chaff . . .	10·5	1·0	5·9	1·25	0·1	2·1	73·6	—	5·5					
	" " " . . .	10·3	0·1	7·5	1·6	0·3	3·95	69·7	—	6·6	7·1	6·65			
	" " " . . .	12·5	0·25	4·9	1·4	0·1	2·3	69·9	—	5·5					
	Hopeton: " " . . .	11·8	—	7·1	1·45	0·7	4·45	60·4	—	5·2					
	" " " . . .	10·0	0·85	5·4	3·3	1·5	5·6	67·2	—	7·05					
	Red straw white: " . . .	12·8	0·7	3·5	3·3	0·1	3·3	70·5	—	5·8					
	" " " . . .	9·5	1·4	7·3	3·5	1·1	2·3	71·5	—	3·4					
	" " " . . .	11·8	—	6·8	3·6	0·5	2·2	66·1	—	8·85					
	" " straw	18·0	2·5	7·4	1·9	0·45	3·1	63·9	—	2·75	—	—	4·2	4·8	
	" " chaff	9·1	1·8	1·9	1·3	0·4	—	81·2	—	4·3					
	BARLEY:														
Way and Ogston.	Chevalier (on clay soil): straw with chaff	11·2	—	5·8	2·7	1·4	1·1	68·5	—	7·2	—	2·1			
	" (on loam soil): "	14·4	0·3	8·5	1·7	0·2	2·2	62·8	1·25	4·2	—	4·4	5·0	5·5	1·02
	" (on lime soil): "	20·2	3·3	11·9	2·9	0·3	3·2	48·2	3·55	3·4		3·1	3·3	3·65	0·54
	Moldavian (on clay soil): "	12·7	2·65	5·3	2·65	1·7	2·7	63·3	—	3·2	—	5·7	6·1	6·8	1·56
	Chevalier: awn	7·7	0·4	10·4	1·3	1·5	3·0	70·8	2·0	2·0	—	1·1	12·1	14·2	
	OATS:														
Way and Ogston.	Potato (on clay soil): straw . . .	21·7	2·6	8·6	5·5	1·1	2·25	19·5	—	5·3	—	3·4	4·7	5·2	1·37
	" (on sandy soil): " . . .	20·6	3·2	7·5	6·6	0·5	3·4	45·6	4·1	7·0	—	4·1	4·8	5·4	2·12
	Hopeton (on sandy soil): straw . .	16·1	—	4·9	2·3	2·7	4·4	53·4	—	2·9	8·1	5·2	4·4	4·95	1·24
	Unknown variety: chaff . . .	13·1	4·1	8·65	2·6	1·4	2·5	59·9	0·2	0·3	—	1·2	7·8	9·2	
J. P. Norton.	Potato: husks	2·2	9·0	4·3	2·35	0·3	4·3	74·2†	—	0·7	—	2·4			
	Hopeton (mean of 3 samples): husks .	5·7	3·93	2·8	0·7	1·7*	6·5	76·4‡	—	1·8	1·4	0·2			

* With 0·8 Mn^4O^3.

† Including 68·4 sand.

‡ Including 73·4 sand.

Way and Ogston deduce from their analyses of the ash of cereals the following general conclusions:

The *amount* of ash is not influenced in any definite manner by the nature of the soil; it appears, however, to be greatest on clay soils, less on calcareous, and least on sandy soils. The strongest straw contains the largest amount of ash. The amount of ash in the chaff varies in proportion to that in the straw, not to that in the grain (see Table I.). The amount of ash in the grain varies between much narrower limits than that of the straw or chaff. It varies as much in different samples of grain grown on the same soil as in samples from different soils, and bears no definite relation either to climate or to variety. But in all cases that were examined, the proportion of ash in the grain was found to vary inversely as the total weight of grain in the crop; whence it would appear that the amount of mineral constituents abstracted from the soil by the grain is the same whatever may be the actual weight of the crop.

Not only the amount, but likewise the composition of the ash appears to be independent of the nature of the soil: the predominance of any constituent, lime or silica, for example, in the soil by no means leads to a predominance of that same constituent in the plant. Neither does it appear that different bases have any tendency to replace one another in plants. An abundance of soda in the soil or the manure does not cause that alkali to take the place of potash in the plant. Other chemists have, however, arrived at different conclusions relating to this point. (See Daubeny, Chem. Soc. Qu. J. v. 9; xiv. 215.—Malaguti and Durocher, Ann. Ch. Phys. [3] liv. 257.)

The difference in the amount of ash in the grain, straw, and chaff relate only to the silica; if this be deducted, the remainders exhibit no perceptible difference.

The ash of the grain of barley and oats differs from that of wheat-grain only in the much larger amount of silica contained in the two former; if this be deducted, all essential differences vanish.

For further details, see the names of the several cereals (BARLEY, under HORDEUM); also the articles SOILS and MANURES.

CEREBRIC ACID. (Frémy, Ann. Ch. Phys. [2] lvi. 168; v. Bibra, *Vergleichende Untersuchungen über das Gehirn der Menschen und der Wirbelthiere*, Mannheim, 1854.)—A fatty acid contained in the brain. It is obtained by cutting brain into thin slices; treating it repeatedly with boiling alcohol to deprive it of water; pressing it; digesting first with cold then with warm ether; distilling off the ether from the solution; and digesting the slimy residue with a much larger quantity of ether. Cerebric acid then remains as a sodium-salt mixed with phosphate of calcium, oleo-phosphoric acid in the form of a sodium and calcium-salt, and brain-albumin. To purify the product, it is digested in boiling absolute alcohol slightly acidulated with sulphuric acid, which leaves the calcium and sodium undissolved as sulphates, while the alcohol takes up the cerebric and oleo-phosphoric acids, and deposits them on cooling. Lastly, the mixture is washed with cold ether, which dissolves the oleo-phosphoric acid and leaves the cerebric acid, which is finally purified by recrystallising it several times from boiling ether.

Cerebric acid has a white, granular, crystalline aspect; it is soluble in boiling alcohol, insoluble in cold ether, easily soluble in boiling ether; in boiling water it swells up, but does not dissolve. It melts at a temperature near that at which it begins to decompose, and when more strongly heated burns with a characteristic odour, leaving a difficultly combustible charcoal with a decided acid reaction. It consists, according to Frémy, of 66·7 per cent. carbon, 10·6 hydrogen, 2·3 nitrogen, 0·9 phosphorus, and 19·5 oxygen. According to Müller and v. Bibra, the phosphorus is not an essential constituent.

Cerebric acid is a weak acid, but nevertheless forms salts with all bases. The *ammonium-*, *potassium-*, and *sodium*-salts are obtained as precipitates, nearly insoluble in alcohol, by placing an alcoholic solution of cerebric acid in contact with the respective alkalis. *Baryta*, *strontia*, and *lime* unite directly with cerebric acid, and deprive it of its property of forming an emulsion with water.

CEREBRIN. This name has been applied to several substances obtained from brain. Fourcroy in 1793 (Ann. Chim. xvi. 283) obtained a substance which was called cerebrin, brain-fat, or phosphoretted bile-fat, and was probably a mixture of Frémy's cerebric acid with the substance which separates after some time from alcohol in which anatomical preparations containing nerves or brain have been preserved. Chevreul applied the same term to a substance obtained from blood-serum, probably a mixture of fats and glycerides containing phosphoric acid. Lastly, Gobley (J. Pharm. [3] xviii. 107) designates as cerebrin, a substance obtained chiefly from carp's eggs, and agreeing essentially in composition and property with Frémy's cerebric acid, excepting that it does not exhibit any tendency to combine with bases.

W. Müller (Ann. Ch. Pharm. cv. 361) has obtained a substance analogous to

Frémy's cerebrin, by triturating brain to a thin pulp with water, heating the mixture to the boiling point, and treating the separated coagulum with boiling alcohol. The alcoholic extract filtered at the boiling heat deposits a mixture of cholesterin and cerebrin, together with other substances; and on treating this mixture with cold ether, cerebrin remains behind, and may be purified by repeated crystallisation from boiling alcohol. It then forms a snow-white powder composed of microscopic spherules, agreeing with Frémy's cerebric acid in most of its properties, especially in swelling up in water like starch, and forming an emulsion. It contains 68·45 per cent. carbon, 11·20 hydrogen, 4·51 nitrogen, and 15·66 oxygen, whence Müller deduces the empirical formula $C^{17}H^{33}NO^{3}$. It does not dissolve in alkalis or in dilute acids, but is decomposed at the boiling heat by hydrochloric, sulphuric, and nitric acid. The product of its decomposition by nitric acid is a non-azotised white waxy body, soluble in alcohol and ether. Treated with strong sulphuric acid in the cold, it dissolves with dark purple-red colour, and the solution mixed with a large quantity of water becomes colourless, and deposits a yellowish, tenacious, flocculent substance.

It is most probable that the cerebrin of Gobley and Müller, the cerebrote of Couerbe, and the cerebric acid of Frémy and v. Bibra contain, as their essential constituent, one and the same substance, which is likewise present in cephalote and stearoconote. (Handw. d. Chem. 2te Aufl. ii. [2] 888.)

CEREBROL (Berzelius). *Eleene-cerebrol* (Couerbe).—An oily reddish substance, insoluble in water, soluble in alcohol and ether, obtained by Couerbe (J. Chim. méd. ii. 765; x. 524) from brain. According to Frémy, it is a mixture of olein, oleo-phosphoric acid, cholesterin, and cerebric acid.

CEREBRO-SPINAL FLUID. A serous fluid contained in the sub-arachnoïdal cavities, and forming a liquid atmosphere round the brain and spinal marrow. It belongs to the class of serous transudates, and is generally distinguished by its very small amount of solid constituents, especially of organic matter. These constituents are albumin, traces of fat, extractive matter, and the inorganic salts of blood-serum. It contains also a substance which reduces cupric salts, but differs from glucose in not being resolved into alcohol and carbonic acid by fermentation. According to F. Hoppe (Chem. Centralbl. 1860, p. 42) this substance is soluble in water and in absolute alcohol, does not crystallise, either *per se* or with chloride of sodium, is not precipitated either by neutral or basic acetate of lead alone, but yields a precipitate with the latter in presence of ammonia. It is decomposed by putrefaction.

Hoppe and Schwaberg analysed the cerebro-spinal fluid obtained by puncturing, in two cases of *Spina bifida* and two of *Hydrocephalus internus*, with the following results:—

	Spina bifida.		Hydrocephalus.	
	I. Puncture.	II. Puncture.	I. Puncture.	II. Puncture.
Water	989·33	989·80	979·01	989·53
Soiled matter	10·67	10·20	20·99	10·47
Albumin	0·25	0·55	11·79	0·70
Extractive matter	2·30	2·00	1·32	1·57
Soluble salts	7·67	7·20	7·54	7·67
Insoluble salts	0·45	0·45	0·35	0·53

The fluids from the *Spina bifida* were strongly alkaline and perfectly transparent. The first reduced cupric oxide, the second did not. The second hydrocephalic liquid also exhibited the reducing action. The greater amount of albumin in the first hydrocephalic liquid was due to previous inflammation of the transudent vessels. (Handw. d. Chem. ii. [2] 891.)

CEREBROTE. (Couerbe, Ann. Ch. Phys. [2] lvi. 164.) *Brain-wax*, *Hirnwachs* (L. Gmelin), *Markpulver*, *Myelocone* (Kühn.)—A substance containing sulphur and phosphorus, which Couerbe obtained by treating the deposit which separates from the alcoholic and ethereal extracts of the brain with ether; cholesterin then dissolves, and the so-called cerebrote remains. According to Frémy, it is merely a mixture of cerebric acid with small quantities of cerebrate of potassium and brain-albumin.

CERIC ACID. An acid obtained by treating cerin, the waxy matter of cork, with nitric acid, washing with water, dissolving in alcohol, filtering and evaporating. It is a brownish diaphanous waxy mass, which softens at a gentle heat, and melts below the boiling point of water. Dissolves readily in alkalis. Yields empyreumatic products when heated. Contains 64·2 per cent. carbon, 8·8 hydrogen, and 27·0 oxygen. With acetate of *lead* it forms a white precipitate containing 51·1 C, 6·9 H, 19·2 $Pb^{2}O$, and 22·8 O. (Döpping, Ann. Ch. Pharm. xlv. 289.)

CERIN. A waxy substance extracted by alcohol or ether from grated cork, previously freed from the outer crust. It separates from the solution in yellowish needles, which may be obtained colourless by recrystallisation. Contains 74·95 carbon, 10·55 hydrogen, and 14·5 oxygen, agreeing nearly with the empirical formula $C^{23}H^{40}O^{3}$. Cerin softens in boiling water and falls to the bottom. It is not attacked by boiling potash. Thrown on glowing coals, it volatilises like beeswax, giving off white fumes. By dry distillation it yields a little acid and a large quantity of an oil which solidifies on cooling; it leaves but little charcoal. Treated with hot nitric acid it yields ceric acid, together with oxalic and carbonic acids. Cork contains from 1·8 to 2·5 per cent. of waxy matter. (Chevreul, Ann. Chim. xcvi. 170; Döpping, *loc. cit.*)

The name *cerin* was also applied by John to the portion of beeswax which is soluble in alcohol; but according to Brodie, the substance thus designated is merely impure cerotic acid (*q. v.*)

CERINE or ALLANITE. See ORTHITE.

CERININ. A waxy fat obtained from the lignite of Gerstewitz near Merseberg, of which it forms about 18 per cent. Contains 76·7 to 78·1 C, and 11·1 to 12·3 H. Plastic at common temperatures; melts at 100° C.; sparingly soluble in alcohol; not saponifiable; yields a crystalline product by distillation. (Wackenroder, Ann. Ch. Pharm. lxxii. 315.)

CERITE. A hydrated silicate of cerium, containing also lanthanum and didymium. It is the chief source of cerium, and is the mineral from which that metal was first obtained. It is found only in an abandoned copper mine at Riddarhytta in Westmanland, Sweden, occurring in compact fine-grained masses of indistinct blackish red colour; also in short six-sided prisms. Specific gravity 4·93. Hardness 5·5. Before the blowpipe it gives off water, but does not melt. It is completely decomposed by hydrochloric acid, leaving a residue of silica. According to Kjerulf (Ann. Ch. Pharm. lxxxvii. 12) it does not give off a trace of chlorine when treated with hydrochloric acid, and consequently the cerium exists in it wholly as cerous oxide. Kjerulf found it to contain:

SiO^{2}	$Ce^{2}O$	$La^{2}O$ $Di^{2}O$	$Fe^{2}O$	$Ca^{2}O$	$H^{2}O$	MoS	BiS	
20·40	56·07	8·12	4·77	1·17	5·29	3·27	0·18	= 99·27

whence may be deduced the formula $2M^{2}O.SiO^{2}$ + aq. or $M^{4}SiO^{4}$ + aq. It generally also contains a small quantity of yttria.

CERIUM. *Symbol* Ce. *Atomic Weight* 46.—This metal, which was discovered in 1803, simultaneously by Klaproth and by Hisinger and Berzelius, exists, together with lanthanum and didymium, in cerite, allanite, orthite, yttro-cerite, and a few other minerals, all of somewhat rare occurrence. The most abundant of them is cerite (*vid. sup.*) To extract the oxides of the three metals, the cerite is finely pounded and boiled for some hours with strong hydrochloric acid, or aqua-regia, which dissolves the metallic oxides, leaving nothing but silica. The filtered solution is then treated with a slight excess of ammonia, which precipitates everything but the lime; the precipitate is redissolved in hydrochloric acid, and the solution treated with excess of oxalic acid. A white or faintly rose-coloured precipitate is then obtained, consisting of the oxalates of cerium, lanthanum, and didymium: it is curdy at first, but in a few minutes becomes crystalline, and easily settles down. When dried and ignited, it yields a red-brown powder, containing the three metals in the state of oxide. The finely pounded cerite may also be mixed with strong sulphuric acid to the consistence of a thick paste, the mixture gently heated till it is converted into a dry white powder. and this powder heated somewhat below redness in an earthen crucible. The three metals are thus brought to the state of basic sulphates, which dissolve completely when very gradually added to cold water; and the solution treated with oxalic acid yields a precipitate of the mixed oxalates, which may be ignited as before.

From the red-brown mixture of the oxides of cerium, lanthanum, and didymium thus obtained, a pure oxide of cerium may be prepared by either of the following processes:—1. The mixed oxides are heated with strong hydrochloric acid, which dissolves the whole, with evolution of chlorine; the solution is precipitated with excess of caustic potash; and chlorine gas passed through the liquid with the precipitate suspended in it. The cerium is thereby brought to the state of ceroso-ceric oxide, which is left undissolved in the form of a bright yellow precipitate, while the lanthanum and didymium remain in the state of protoxides, and dissolve. To ensure complete separation, the passage of the chlorine must be continued till the liquid is completely saturated with it, and the solution, together with the precipitate, left for several hours in a stoppered bottle, and agitated now and then. The liquid is then filtered, the washed precipitate treated with strong boiling hydrochloric acid, which dissolves it with evolution of chlorine, and forms a colourless solution of protochloride of cerium; and this, when treated with oxalic acid or oxalate of ammonia, yields a perfectly white precipitate of oxalate of cerium, which may be converted into oxide by ignition (Mosander).—2. The red-brown mixture of the three oxides is treated with very dilute nitric acid (1 pt. of nitric acid of ordinary strength to between 50 and 100 pts. of water), which dissolves the greater part of the oxides of lanthanum and didymium, and leaves the oxide of cerium; and by treating the residue with very strong nitric acid, the last traces of lanthanum and didymium may be extracted (Mosander, Marignac).—3. The red-brown mixture of the three oxides is boiled for several hours in a strong solution of chloride of ammonium. The oxides of lanthanum and didymium then dissolve, with evolution of ammonia, and sesquioxide of cerium is left in a state of purity. It must be collected on a filter and washed with a solution of sal-ammoniac, because, when washed with pure water, it first runs through the filter, and then stops it up (Watts, Chem. Soc. Qu. J. ii. 147).—4. Oxalate of cerium obtained as above is mixed with half its weight of pure magnesia, and made up into a stiff paste with water; and this mixture when dry is heated to low redness in a porcelain basin, with constant stirring. The product is a cinnamon-coloured powder, containing the whole of the cerium as ceric (? ceroso-ceric) oxide, in combination with magnesia, oxide of lanthanum, and other protoxides. It dissolves completely, with aid of heat, in strong nitric acid, forming a deep brown solution of a double salt, which appears to consist of ceric nitrate in combination with cerous nitrate and the nitrates of lanthanum, didymium, and magnesium, sometimes also a small quantity of nitrate of yttrium. This double salt separates in splendid rhombohedral crystals having nearly the colour of acid chromate of potassium. The solution, if diluted with water before these crystals have separated, does not yield any precipitate, either in the cold or in boiling; but if the crystallisation be allowed to go on till lighter-coloured laminated crystals separate containing magnesium and lanthanum with very little cerium, the mother-liquor then deposits, on dilution and boiling, a basic salt of cerium free from all other metals. The precipitate is not formed so long as the red double salt remains dissolved in the liquid; indeed it redissolves on adding to the liquid a solution of that salt. The liquid from which the cerium precipitate has separated still retains cerium, which may be separated by repetition of the treatment.

To separate the cerium from the solution of the red salt, it is diluted with a large quantity of water, then boiled, and sulphuric acid added in small quantity as long as the resulting precipitate is thereby increased. The cerium is then precipitated as a yellowish-white, flocculent basic salt, containing both nitric and sulphuric acids, but free from all other metals, which is difficult to wash on a filter, but is easily washed by decantation with water slightly acidulated with sulphuric acid. This salt dissolves readily in strong sulphuric acid, and the solution, after reduction with sulphurous acid, yields, with oxalic acid, a white precipitate of pure cerous oxalate.

If it be desired to obtain a basic nitrate of cerium free from sulphuric acid, as is often desirable for other preparations, the red solution of the double nitrate must be evaporated to a syrup, and then poured into a large excess of boiling water slightly acidulated with nitric acid. The precipitate thereby formed is washed by decantation with water containing a little nitric acid, and the mother-liquor, together with the wash-water, is again evaporated to a syrup and treated as before, till nearly all the cerium is extracted. The addition of nitric acid to the wash-water is essential, as the basic nitrate dissolves somewhat readily in pure water. It is best to preserve the precipitated salt under acidulated water, since it becomes insoluble in acids when dried and ignited. (Bunsen, Ann. Ch. Pharm. cv. 40.)

Metallic cerium is obtained by heating the pure anhydrous protochloride with potassium or sodium. It is a grey powder, which acquires the metallic lustre by pressure. It oxidises readily, decomposes water slowly at ordinary temperatures, quickly at the boiling heat, and dissolves rapidly in dilute acids, with evolution of hydrogen, forming a solution of a cerous salt.

Cerium forms three classes of compounds, viz. the *cerous compounds*, or *proto-compounds*, *e.g.* the protochloride, CeCl, the protoxide Ce^2O; the *sesqui-compounds*, or *ceric compounds*, *e.g.* Ce^2Cl^3, and Ce^4O^3, and the *ceroso-ceric* compounds, which may be regarded as compounds of the other two; *e.g.* ceroso-ceric oxide, $Ce^3O^2 = Ce^2O.C^4O^3$.

CERIUM, BROMIDE OF. Not known in the anhydrous state. A solution of ceric oxide in hydrobromic acid yields by evaporation, small crystals of a hydrated bromide, which gives off hydrobromic acid when heated and leaves an oxybromide.

CERIUM, CHLORIDES OF. Cerium burns vividly when heated in chlorine gas, and forms the *protochloride* CeCl. The anhydrous chloride may be prepared by igniting the sulphide, or the residue obtained by evaporating to dryness a solution of the chloride mixed with sal-ammoniac, in a current of chlorine gas. If the air is not completely excluded, an oxychloride is also produced. The anhydrous chloride is a white porous mass, fusible at a red heat, and perfectly soluble in water. A *hydrated* *chloride* is obtained in colourless four-sided prisms, by dissolving the hydrated oxide or the carbonate in hydrochloric acid, and evaporating to a syrup. The solution when exposed to the air, turns yellow, from formation of a ceroso-ceric salt.

Protochloride of cerium forms with *dichloride of platinum*, an orange-coloured crystalline double salt, $2CeCl.PtCl^2.4H^2O$, easily soluble in water and alcohol, insoluble in ether. It also combines with *iodide of zinc*. (Holzmann, Phil. Mag. [4] xxii. 219.)

Ceroso-ceric chloride.—Hydrated ceroso-ceric oxide dissolves in cold hydrochloric acid, forming a red solution, which, however, soon gives off chlorine, and is reduced, more or less completely, to protochloride.

CERIUM, DETECTION AND ESTIMATION OF. 1. *Reactions.*—All compounds of cerium, ignited with *borax* or *microcosmic salt* in the outer blowpipe flame, yield a glass which is deep red while hot, but becomes colourless on cooling. In the inner flame, a colourless bead is formed with a small quantity of the cerium compound; but a yellow enamel with a larger quantity.

Cerous salts in solution are colourless, have a sweet astringent taste, and redden litmus, even when the acid is perfectly saturated. They are distinguished by the following reactions: *Sulphydric acid* produces no precipitate. *Sulphide of ammonium* throws down the hydrated protoxide. *Caustic potash* or *soda* produces a white precipitate of the hydrated protoxide, which is insoluble in excess, and is converted into the yellow hydrated sesquioxide by the action of chlorine-water or hypochlorous acid. *Ammonia* precipitates a basic salt. *Alkaline carbonates* form a white precipitate of cerous carbonate insoluble in excess. *Oxalic acid* or *oxalate of ammonia* produces a white precipitate of cerous oxalate, gelatinous at first, but quickly assuming the crystalline character, and converted by ignition in an open vessel into a yellowish-white powder consisting of ceroso-ceric oxide. *Ferrocyanide of potassium* produces a white pulverulent precipitate; ferricyanide of potassium none. *Sulphate of potassium* produces a white crystalline precipitate of potassio-cerous sulphate, nearly insoluble in pure water, and quite insoluble in excess of sulphate of potassium. With dilute solutions the precipitate takes some time to form. This character, together with the behaviour of the oxalate and the yellow coloration of the hydrated protoxide by hypochlorous acid, serves to distinguish cerium from all other metals.

2. *Quantitative Estimation.*—Cerium is precipitated from neutral solutions of cerous salts by carbonate of ammonium, as cerous carbonate, or by oxalate of ammonium as cerous oxalate; and either of these compounds is converted by ignition in an open vessel, into ceroso-ceric oxide, which, according to Bunsen, corresponds, *within the limits of experimental error*, to the formula Ce^3O^4, and contains 81·18 per cent. of metallic cerium, or 95·04 per cent. of the protoxide. Another method is to dissolve the precipitated carbonate in dilute sulphuric acid, evaporate, and heat the residue to commencing redness, whereby it is converted into the anhydrous sulphate, Ce^2SO^4, containing 48·95 per cent. of the metal, or 57·45 per cent. of the protoxide.

3. *Separation from other Elements.*—Sulphydric acid serves to separate cerium from all metals which are precipitated by that reagent from their acid solutions. From *manganese*, *iron*, *cobalt*, *nickel*, *zinc*, *titanium*, *chromium*, *vanadium*, and *tungsten*, cerium may be separated by means of a saturated solution of sulphate of potassium.

From *aluminium* it may be separated by carbonate of barium, which precipitates alumina and not cerous oxide; from *glucinum* by sulphate of potassium. From *yttrium*, with which it is often associated in minerals, it may be separated by a saturated solution of sulphate of potassium, added in excess, the sulphate of yttrium and potassium being soluble in excess of sulphate of potassium, while the cerous double salt remains undissolved. From *zirconium*, cerium is separated by treating the boiling acid solution with sulphate of potassium, whereby the greater part of the zirconia is precipitated as basic sulphate, while the cerium remains dissolved; to complete the precipitation, a small quantity of ammonia must be added, but not sufficient to saturate the acid (H. Rose). From *magnesium* also cerium may be separated by sulphate of potassium; from *barium*, *strontium*, and *calcium*, it is separated by ammonia added in slight excess; or from barium by sulphuric acid, and from strontium and calcium by sulphuric acid and alcohol; and from the *alkali-metals* by precipitation with oxalate of ammonia. Bunsen's method of precipitation already described, affords however the the best means of separating cerium from all the metals with which it is found associated, especially from *lanthanum*, *didymium*, and *yttrium*.

4. *Atomic Weight of Cerium.*—The older statements respecting the atomic weight of this metal, all refer to cerium containing lanthanum and didymium. For this impure metal, Hisinger, in 1814, found the number 45·65 ($H = 1$), and Otto found 46·8. After the method of removing the lanthanum and didymium had been pointed out by Mosander, Beringer (Ann. Ch. Pharm. lii. 134), from the analysis of the proto-

chloride CeCl, deduced the number 47·8, and from that of the sulphate the number 46·2.

Hermann, from an analysis of cerous sulphate, in which the sulphuric acid was precipitated as sulphate of barium, found for cerium the number 46.

Marignac (Ann. Ch. Pharm. lxviii. 215), by precipitating cerous sulphate with a graduated solution of chloride of barium, obtained, as a mean of seven experiments, Ce = 47·26. Afterwards, however (Ann. Ch. Phys. [3] xxxviii. 148), he rejected this number, and adopted that previously found by Hermann, viz. 46, attributing the excess of his former determination to the circumstance, that a portion of the cerous sulphate had been carried down undecomposed by the barium precipitate, whence the quantity of chloride of barium required to precipitate the sulphate came out too low.

Lastly, Bunsen has determined the atomic weight of cerium by the analysis of the sulphate. Pure basic ceric sulphate, obtained as above described (p. 832), was dissolved in sulphuric acid, reduced to cerous sulphate by sulphurous acid, the salt evaporated and ignited till all the excess of acid was expelled, and the residue twice crystallised from water. A solution of this salt was precipitated by oxalic acid; the precipitated oxalate converted into ceroso-ceric oxide by ignition in an open vessel; and the sulphuric acid precipitated from the filtrate by chloride of barium. The ceroso-ceric oxide was then heated in a sealed flask containing very little air, with pure hydrochloric acid and iodide of potassium, whereby it was reduced to cerous oxide, and a quantity of iodine set free equivalent to the oxygen separated from the ceroso-ceric oxide. This free iodine was estimated by Bunsen's volumetric method (ANALYSIS, VOLUMETRIC, p. 266), and the corresponding amount of oxygen estimated by the formula $x = \frac{O}{2I}\ a\ (nt - t')$. In this manner, 100 pts. of the ceroso-ceric oxide were found to contain 95·04 cerous oxide and 4·96 oxygen. From this, the quantity of cerous oxide in the ignited ceroso-ceric oxide (that is to say, in the original quantity of cerous sulphate), was calculated, and the amount of sulphuric acid (SO^3) being likewise found from the precipitated sulphate of barium, the composition of the cerous sulphate was found to be $57·49\ Ce^2O + 42·51\ SO^3 = 100$, whence the atomic weight of cerous oxide was found from the proportion $42·51 : 57·49 = 80 : x$, giving $Ce^2O = 108·1$, and therefore $Ce = 46·1$. Two other experiments gave $Ce = 46·02$ and $46·05$.

In accordance with the preceding results, the whole number 46 is generally adopted as the true atomic weight of cerium.

CERIUM, FLUORIDES OF. The protofluoride CeF, is obtained as a white precipitate, by adding an alkaline fluoride to a cerous salt. It is but partially reduced by the action of hydrogen gas and potassium vapour at a red heat. (Mosander.)

The *sesquifluoride*, Ce^2F^3, prepared in like manner, is a yellow precipitate. It also occurs native as *fluocerite*, in brick-red or nearly yellow six-sided prisms and plates, with very distinct basal cleavage; also massive; specific gravity 4·7. Hardness 4·5. It gives off fluorine when strongly heated in a glass tube. It occurs at Finbo and Broddbo, near Fahlun, in Sweden. Sesquifluoride of cerium also occurs with the fluorides of calcium and yttrium, as *yttrocerite* (*q. v.*)

A *hydrated ceric oxyfluoride*, $Ce^6F^6O^3 + 3H^2O$, occurs at Finbo as *fluocerine*, in yellow crystals with vitreous lustre, supposed to belong to the regular system (Gm. iii. 271). A mineral from Bastnäs in Sweden, analysed by Hisinger, yielded numbers corresponding to the formula $Ce^6F^6O^3 + 4H^2O$; one from Finbo, analysed by Berzelius, was found to consist of $Ce^{16}F^6O^9 + 3H^2O$, or $2Ce^2F^3.3(Ce^4O^3.H^2O)$. (Dana, ii. 96.)

CERIUM, OXIDES OF. The *Protoxide*, or *Cerous oxide*, Ce^2O, is obtained by heating the carbonate or oxalate in a current of dry hydrogen perfectly free from air. It is a greyish-blue powder, which on exposure to the air quickly becomes very hot, and is converted into yellowish-white ceroso-ceric oxide. *Cerous hydrate* precipitated from the solution of a cerous salt by a caustic alkali, is white, but when exposed to the air, quickly changes to a yellow mixture of cerous carbonate and ceroso-ceric hydrate (Rammelsberg, Pogg. Ann. cviii. 40). The hydrate dissolves readily in sulphuric, nitric, hydrochloric, and acetic acid, the solutions giving the characters described at p. 833.

Ceroso-ceric Oxide, Ce^3O^2.—This oxide, which may be regarded as a compound of cerous and ceric oxide: $2Ce^3O^2 = Ce^2O.Ce^4O^3$, is produced when cerous hydrate, carbonate, oxalate, or nitrate, is ignited in an open vessel. It is yellowish-white, acquires a deep orange-red colour when heated, but recovers its original tint on cooling (Bunsen, Rammelsberg). Ignited in hydrogen gas, it assumes an olive-green colour, but does not diminish perceptibly in weight (Bunsen). It is not raised to a higher state of oxidation by heating in oxygen gas, or even by fusion with chlorate or hydrate of potassium (Rammelsberg). Nitric and hydrochloric acid have but little action upon it, even at the boiling heat, unless it be mixed with the oxides of lanthanum and didymium, in which case it dissolves readily in hot hydrochloric acid, with evolution of chlorine. Heated with a mixture of iodide of potassium and hydrochloric acid, it dissolves completely, with separation of iodine,—a property which has been made available by Bunsen for determining its composition. Strong sulphuric acid at the boiling heat, converts it into an orange-red salt, which becomes light yellow on cooling, and dissolves with yellow colour in water.

Marignac did not obtain ceroso-ceric oxide of constant composition, but supposed it to have, for the most part, the composition $3Ce^2O.2Ce^4O^3$, or $Ce^{14}O^9$. Rammelsberg, by decomposing the ceroso-ceric sulphate, $3Ce^2SO^4.Ce^4(SO^4)^3$ with potash, obtained a reddish-grey precipitate which contained $3Ce^2O.Ce^4O^3$, but was quickly converted into Ce^3O^3, on exposure to the air.

Ceroso-ceric Hydrate, $2Ce\,O^2.3H^2O$, obtained by passing chlorine into aqueous potash in which cerous hydrate is suspended (p. 831), is a bright yellow precipitate, which dissolves readily in sulphuric and nitric acid, forming yellow solutions of ceroso-ceric salts; in hydrochloric acid, with evolution of chlorine, forming colourless cerous chloride.

Ceric Oxide, Ce^4O^3, does not appear to exist in the free state, inasmuch as ceroso-ceric oxide is not brought to a higher state of oxidation, even by ignition with powerful oxidising agents (*vid. sup.*)

CERIUM, OXYGEN-SALTS OF. The *cerous salts* are produced by dissolving cerous oxide or carbonate in acids, also by the action of sulphurous acid and other reducing agents on ceric or ceroso-ceric salts. (For their properties and reactions see p. 833.) Cerous silicate exists in nature as *Cerite;* the phosphate as *Monazite*, *Erdwardsite*, *Cryptolite*, and *Phosphocerite:* the carbonate, together with fluoride of calcium, in *Parisite.*

Cerous sulphate forms sparingly soluble double salts with the sulphates of ammonium, potassium, and sodium. The potassium-salt, $KCeSO^4$, is the least soluble in water, and quite insoluble in solution of sulphate of potassium.

The *ceroso-ceric* salts are obtained by dissolving the corresponding oxide or hydrate in acids. The solution of the sulphate yields by spontaneous evaporation, first brown-red crystals, composed of $3Ce^2SO^4.Ce^4.(SO^4)^3 + 18\,aq.$, and afterwards a yellow, indistinctly crystalline salt, containing $Ce^2SO^4.Ce^4(SO^4)^3 + 8\,aq.$ By substituting *cericum*, $ce = 30\frac{2}{3}$ for *cerosum*, $Ce = 46$, in the sesquisulphate, these formulæ may be reduced to $\left.\begin{matrix}(SO^2)''\\ Ce\,.\,ce\end{matrix}\right\}O + 6\,aq.$ and $\left.\begin{matrix}(S^2O^4)^{iv}\\ Ce.ce^3\end{matrix}\right\}O^4 + 4\,aq.$, respectively. Both salts are decomposed by water, with separation of a basic salt, containing $5Ce^2O^2.3\left(\left.\begin{matrix}S^2O^4\\ Ce\,.\,ce\end{matrix}\right\}O^4\right)$ $+ 12\,aq.$, but dissolve on addition of sulphuric or nitric acid. The solution of either salt yields, with sulphate of potassium, a mixture of at least two double salts, in which potassium and cerosum may be regarded as replacing one another isomorphously: similarly with sulphate of ammonium: the ammonium double salts, when ignited, leave pure ceroso-ceric oxide.

The rhombohedral nitrate of cerium and magnesium obtained by Bunsen (p. 832), is, when purified, a ceroso-cerico-magnesic salt, containing $Mg^2Ce(NO^3)^3.(Ce^2)'''(NO^3)^3$ $+ 8\,aq.$, or $\left.\begin{matrix}(NO^2)^6\\ Mg^2\,Ce\,ce^3\end{matrix}\right\}O^6 + 8\,aq.$ [As originally obtained, it contains lanthanum and didymium, replacing cerium isomorphously.] Double salts of similar composition are obtained by mixing a solution of this nitrate with the nitrates of potassium and zinc; with nitrate of nickel, a basic salt containing $\left.\begin{matrix}(NO^2)^6\\ Ni^2\,Ce\,ce^3\end{matrix}\right\}O^6.NiHO + 12H^2O$. (Holzmann, J. pr. Chem. lxxv. 321.)

The existence of pure *ceric* salts is by no means certain. Bunsen speaks of a basic ceric sulphate, precipitated by boiling the solution of the magnesian ceroso-ceric salt just mentioned, with sulphuric acid; but he has not given an analysis of it: indeed, *no analysis of a pure ceric salt has yet been published.* The so-called basic ceric sulphate just mentioned, yields, by digestion with caustic potash, not ceric, but ceroso-ceric hydrate (Holzmann). [For further details respecting the oxygen-salts of cerium, see the several acids.]

CERIUM, PHOSPHIDE OF. Said to be obtained, together with phosphate, by passing phosphoretted hydrogen over white-hot ceroso-ceric oxide. (Mosander.)

CERIUM, SELENIDE OF. Produced by decomposing cerous selenite with hydrogen at a red heat. It is a brownish powder, which dissolves in acids, with evolution of selenhydric acid. Cerous salts give with alkaline selenides a pale red precipitate, probably consisting of hydrated selenide of cerium.

CERIUM, SULPHIDES OF. *Cerous sulphide*, Ce^2S, is obtained by igniting the carbonate in vapour of sulphide of carbon, or by heating an oxide of cerium with sulphide of potassium. The first process yields a light powder of the colour of red lead; the second, a product resembling mosaic gold (Mosander). *Ceric sulphide* is not known in the free state, but is said to combine with other metallic sulphides.

CEROLEIN. A substance obtained from beeswax (in which it is said to exist to the amount of 4 or 5 per cent.) by treating the wax with boiling alcohol, leaving the cerotic acid to deposit on cooling, and evaporating the filtered solution. It is very soft, melts a 28·5° C., dissolves readily in cold alcohol and ether; is acid to litmus; gives by analysis 78·74 per cent. C, 12·51 H, and 8·75 O (Lewy, Ann. Ch. Phys. [3] xiii. 438). It is probably a mixture.

CEROLITE or **KEROLITE** (from κηρος wax, and λιθος stone).—This name is applied to two or three minerals or mixtures, consisting chiefly of hydrated silicate of magnesium more or less mixed with silicate of aluminium. They are all massive, reniform, compact or lamellar, transparent or translucent, white or grey, with vitreous or resinous lustre, and greasy to the touch.

Analyses.—*a.* From Frankenstein in Silesia by Kühn; *b.* from an unknown locality by Delesse; *c.* from Zöblitz in Saxony by Melling:

	SiO^2	Al^4O^3	Mg^2O	Fe^2O	H^2O	
a . .	46·96	—	31 26	—	21·22	= 99·44
b . .	53·5	0·9	28·6	—	16·4	= 99·4
c . .	47·13	2·57	36·13	2·92	11·50	= 100·25

The first agrees nearly with the formula $Mg^4SiO^4 + 3aq.$ (*Rammelsberg's Mineralchemie*, p. 862.)

CEROPIC ACID. An acid obtained by Kawalier (Ann. Ch. Pharm. lxxxviii. 360) from the needles of the Scotch fir (*Pinus sylvestris*). The needles are boiled with alcohol of 40 per cent., the alcohol is distilled off, and the residue is mixed with water, whereby it is separated into a yellowish resin and a somewhat turbid liquid. The resinous mass is redissolved in alcohol of 40 per cent., the solution precipitated with acetate of lead, and the precipitate suspended in alcohol is decomposed by sulphuretted hydrogen. The solution filtered hot deposits ceropic acid in yellowish-white flocks, which, by boiling with alcohol and animal charcoal and repeated crystallisation from alcohol, may be obtained in white, friable, microscopic crystals, melting at 100° C., and solidifying in a waxy mass. The crystals dried in vacuo gave by analysis 74·24 per cent. carbon and 12·17 hydrogen, whence Kawalier deduces the improbable formula $C^{36}H^{34}O^{5}$. The barium-salt gave 65·50 carbon, 10·33 hydrogen, 12·65 oxygen, and 11·52 baryta, represented by the formula $BaO.C^{36}H^{34}O^{5}$.

CEROSIC ACID. $C^{48}H^{96}O^{2}$.—Obtained by heating cerosin (sugar-cane wax) with potash-lime, and purified by saponifying with baryta, dissolving the soap in alcohol, decomposing it with hydrochloric acid, and dissolving the precipitate in rock-oil, whence it crystallises on cooling. It melts at 93°C.; dissolves sparingly in boiling alcohol and ether. (Lewy, Ann. Ch. Phys. [3] xiii. 438.)

CEROSIN. *Cerosie.*—The wax of the sugar-cane, obtained by rasping the bark of the cane, especially of the violet variety, and purified by recrystallising several times from boiling alcohol. It then forms delicate white nacreous laminæ, which do not stain paper. Gives by analysis 81·0 to 81·7 C and 13·6 to 14·2 H, agreeing nearly with the formula $C^{48}H^{96}O^{2}$, which represents it as a kind of aldehyde or ether. It melts at 82° C., is insoluble in cold ether and alcohol, very soluble in boiling alcohol. It is very hard and easily pulverised. (Avequin, Ann. Ch. Phys. lxxv. 218; Dumas, *ibid.* lxxv. 222; Lewy, *loc. cit.*)

CEROTENE. $C^{27}H^{54}$.—A hydrocarbon homologous with ethylene, first obtained by Brodie (Phil. Mag. [3] xxxiii. 378; Ann. Ch. Pharm. lxvii. 199) as a product of the dry distillation of Chinese wax. The distillate consists of two parts, cerotic acid passing over first, and afterwards cerotene mixed with a certain quantity of oily matter, which may be removed by pressure. It is purified by crystallisation, first from a mixture of alcohol and naphtha, then from ether. It is crystalline, melts between 57° and 58° C., and exhibits the characters of the substances which have been confounded under the name of *Paraffin* (*q. v.*) When distilled several times, it is completely transformed into a mixture of liquid hydrocarbons, whose boiling points vary from 75° to 260° C.

Chlorinated derivatives of Cerotene.—When moist chlorine is passed over melted cerotene, the latter assumes a waxy aspect, then becomes gummy, and is ultimately converted into a transparent resin, becoming harder as it absorbs more chlorine. The reaction takes several weeks to complete, and at different stages of it the following compounds are formed:—$C^{27}H^{36}Cl^{18}$; $C^{27}H^{33}Cl^{21}$; $Cl^{27}H^{32}Cl^{22}$. (Brodie.)

CEROTIC ACID. $C^{27}H^{54}O^{2} = C^{27}H^{53}O.H.O.$ *Cerin of Beeswax.* (John, *Chemische Schriften*, iv. 38; Boudet and Boissenot, J. Pharm. xiii. 38; Ettling, Ann.

Ch. Pharm. ii. 267; Hess, *ibid.* xxvii. 3; Gerhardt, Rev. scient. xix. 5; Lewy, Ann. Ch. Phys. [3] xiii. 438; Brodie, Ann. Ch. Pharm. lxvii. 180.)—This acid is the essential constituent of that portion of beeswax which is soluble in boiling alcohol. It is prepared by treating beeswax several times in succession with boiling alcohol, till the deposit which forms on cooling melts at 70° or 72° C. The acid thus obtained is not yet pure. It is, therefore, to be dissolved in a large quantity of boiling alcohol and the solution precipitated by acetate of lead. The precipitate, after being exhausted with the aid of heat by alcohol and ether, is decomposed by concentrated acetic acid, and the product crystallised from alcohol yields pure cerotic acid. Cerotic acid may also be obtained very nearly pure by crystallising several times from ether, the crude product which melts at 72° C. The mother-liquors retain a small quantity of another fatty acid.— Cerotic acid is likewise produced by the dry distillation of Chinese wax, and by melting that substance with potash.

Pure cerotic acid crystallises on cooling from its solutions in small grains, melting at 78° C. The melted mass assumes on cooling a highly crystalline character.

The pure acid distils without alteration, but the impure acid is decomposed by distillation, yielding principally oily hydrocarbons of very variable boiling point, and containing in solution small quantities of a fatty acid and other oxygenised products. Chlorine transforms cerotic acid into *chlorocerotic acid*, $C^{27}H^{42}Cl^{12}O^2$.

Cerotates.—Cerotic acid is monobasic, the formula of its neutral salts being $C^{27}H^{53}M.O^2$. The *lead-salt*, $C^{27}H^{53}PbO^2$, is obtained as a white bulky precipitate on mixing a solution of cerotic acid in boiling alcohol with alcoholic acetate of lead. The *silver-salt*, $C^{27}H^{53}AgO^2$, is obtained by precipitating an alcoholic and ammoniacal solution of cerotic acid with nitrate of silver at the boiling heat.

CHLOROCEROTIC ACID. $C^{27}H^{42}Cl^{12}O^2$.—Produced by exposing melted cerotic acid to the action of chlorine for several days, as long indeed as fumes of hydrochloric acid are perceptible. The product is a thick transparent gum of a pale yellow colour.

Chlorocerotate of sodium is nearly insoluble in water.

Chlorocerotate of ethyl, $C^{29}H^{46}Cl^{12}O^2 = C^{27}H^{41}Cl^{12}O^2.C^2H^5$, is prepared similarly to the cerotate. It has the aspect of chlorocerotic acid.

CEROTIC ETHERS. *Cerotate of ethyl*, $C^{29}H^{58}O^2 = C^{27}H^{53}O^2.C^2H^5$, is easily produced by passing hydrochloric acid gas into solution of cerotic acid in absolute alcohol. It has the aspect of beeswax, and melts at 59°—60° C.

Cerotate of Ceryl. Chinese Wax. $C^{54}H^{108}O^2 = \left.\begin{matrix}C^{27}H^{53}O\\C^{27}H^{55}\end{matrix}\right\}O$. — This is a peculiar waxy substance obtained from China, where it is produced on certain trees by the puncture of a species of *coccus*. It is crystalline, and of a dazzling whiteness, like spermaceti, but more brittle and of a more fibrous texture. It melts at 82° C. It is purified by crystallisation from a mixture of alcohol and naphtha, then washed with ether, treated with boiling water, and recrystallised from absolute alcohol, which dissolves it in small quantity only. Chinese wax is not saponified completely by boiling with aqueous potash, but decomposes readily when fused with potash, yielding cerotate of potassium and hydrate of ceryl. By dry distillation it yields cerotic acid and cerotene. Almost all the wax gathered in China is used there for making candles. It is also employed by the Chinese as a medicine.

CEROTIN. Syn. of CERYLIC ALCOHOL or HYDRATE OF CERYL (p. 838).

CEROTINONE. The acetone of cerotic acid, obtained by careful distillation of cerotate of lead. (Bruckner, J. pr. Chem. lvii. 1.)

CEROXYLIN or *Palm wax* is the produce of the *Ceroxylon Andicola*, and is obtained by rasping the epidermis of the tree and boiling the raspings in water. The wax floats on the surface in a soft state, while the impurities sink to the bottom. It may be further purified by repeated boiling with alcohol. In its natural state it is a greyish-white powder; after purification, yellowish-white. It is nearly insoluble in alcohol, and melts at 72° C. It has been analysed by Boussingault (Ann. Ch. Phys. xxix. 333), Lewy (Ann. Ch. Phys. [3] xiii. 458), and Teschemacher (Ann. Ch. Pharm. lx. 270) with the following results:—

	Boussingault.	Lewy.	Teschemacher.
Carbon	80·48	80·73	80·28
Hydrogen	13·29	13·30	13·20
Oxygen	6·23	5·97	6·42
	100·00	100·00	100·00

CERUMEN OF THE EAR. A yellow secretion which lines the external auditory canal, rendered viscid and concrete by exposure to air. It has a bitter taste, melts at a low heat, and evolves a slightly aromatic odour. On ignited coals it gives out a white smoke, similar to that of burning fat, swells, emits a fetid ammoniacal odour, and is converted into a light charcoal. Alcohol dissolves ⅝ of it, and on evaporation leaves a substance resembling the resin of bile. The ⅜ which remain are albumin mixed with oil, which by incineration leave carbonate of sodium and phosphate of calcium. U.

CERUSE or *White lead.* See CARBONATES (p. 786).

CERUSITE. Native carbonate of lead (p. 786).

CERVANTITE. Native tetroxide of antimony, SbO^2 or $Sb^2O^3.Sb^2O^5$, found at Cervantes in Spain and at Pereta in Tuscany (p. 324).

CERYL, HYDRATE OF. *Cerylic Alcohol, Cerotin.* $C^{27}H^{56}O = \left.\begin{matrix}C^{27}H^{55}\\H\end{matrix}\right\}O.$ — Produced by fusing Chinese wax (cerotate of ceryl) with potash, digesting the fused mass in boiling water, whereby a solution of cerotate of potassium is obtained holding cerylic alcohol in suspension; precipitating the cerotic acid with chloride of barium; and dissolving out the hydrate of ceryl with alcohol, ether, or coal-tar oil. The hydrate of ceryl, purified by several crystallisations from ether or alcohol, forms a waxy substance melting at 97° C. Heated with potash-lime, it gives off hydrogen, and is converted into cerotate of potassium:

$$C^{27}H^{56}O + KHO = C^{27}H^{53}KO^2 + 4H.$$

At a very high temperature it distils partly undecomposed, partly resolved into water and cerotene, $C^{27}H^{54} + H^2O$. Chlorine acts upon hydrate of ceryl, producing a transparent pale-yellow substitution-product, *chlorcerotal*, containing 37·62 to 37·89 C, 4·76 to 4·78 H, and 55·11 to 55·07 Cl, numbers which correspond to the formula $C^{27}H^{42\frac{1}{2}}Cl^{13\frac{1}{2}}O$. The action of the chlorine was probably not complete. The product has the appearance of a gum-resin, and becomes electrical by friction. (Brodie, Ann. Ch. Pharm. lxvii. 120.)

Hydrate of ceryl treated with excess of sulphuric yields a product which, when washed with cold water, dried in vacuo, and crystallised from ether, has the composition of *neutral sulphate of ceryl with* 1 *at. water*, $(C^{27}H^{55})^2SO^4 + H^2O$. When pure it is perfectly soluble in water, especially if a little alcohol is added; the solution evaporated at a low temperature leaves the substance in the form of a soft wax. (Brodie.)

CETENE or *Cetylene*, $C^{16}H^{32}$. (Dumas and Péligot, Ann. Ch. Phys. [2] lxii. 4; Smith, *ibid.* [3] vi. 40.)—A hydrocarbon homologous with ethylene, obtained by distilling cetylic alcohol with phosphoric anhydride, also by distilling cetin (palmitate of cetyl), and treating the product with potash to saponify the fatty acids which have passed over in the distillation, the cetene then floating on the surface of the liquid.

Cetene is a colourless oily liquid, which stains paper. It boils at 275° C., distilling without alteration. Vapour-density 8·007. It is insoluble in water, easily soluble in alcohol and ether, neutral to test-paper. It has no particular taste. When set on fire, it burns with a very pure white flame, like the fat oils.

Cetene unites with hydrobromic and hydrochloric acids, slowly at ordinary temperatures, somewhat more quickly at 100° C. The compound is decomposed by distillation. (Berthelot, Ann. Ch. Phys. [3] li. 81.)

The ethylosulphates (sulphovinates) yield by dry distillation an oily liquid (*heavy* oil of wine), from which water separates an oily hydrocarbon (*light oil of wine*), which boils at nearly the same temperature as cetene; and this oil, when exposed to a very low temperature deposits crystals (*camphor* or *stearoptene of wine-oil*), having the same composition.

CETIC ACID. $C^{15}H^{30}O^2$?—Produced, according to Heintz, in very small quantity in the saponification of spermaceti (p. 840). Crystallises in nacreous scales grouped in stars, melting at 53·5° C. Benic acid obtained from oil of ben, and stillistearic acid, from the fruit of *Stillingia sebifera*, have the same composition.

CETIN, $C^{32}H^{64}O^2$. (Chevreul, *Recherches sur les Corps gras*, p. 171; Smith, Ann. Ch. Pharm. xlii. 247; Stenhouse, J. pr. Chem. xxvii. 253; Radcliff, Ann. Ch. Phys. [3] vi. 50.)—A fatty crystalline substance constituting the essential part of spermaceti, the substance which, in the state of solution in an oil, fills the cavities in the head of the cacholot, or spermaceti whale, and other cetaceous animals. To obtain it in a state of purity, spermaceti is treated with cold alcohol, which removes the oil, and the residue is crystallised from boiling alcohol.

Cetin melts at 49° C., and solidifies on cooling in a translucent mass, which serves for the manufacture of candles. Heated to 360°, out of contact with the air, it volatilises without alteration; but if heated quickly and in considerable quantities, it is completely decomposed into a solid fatty acid (palmitic acid), and a liquid hydrocarbon (cetene), accompanied, chiefly towards the end of the distillation, by secondary products, such as water, carbonic anhydride, carbonic oxide, and olefiant gas. Cetin is insoluble in water. 100 pts. of *alcohol* of 0·821 dissolve 2·5 pts. of it; *absolute alcohol* and *ether* dissolve it in larger quantities, and deposit it on cooling in brilliant laminæ. *Nitric acid* attacks it slowly, and converts it into a mixture of œnanthylic, adipic, and pimelic acids.

Cetin boiled with caustic alkalis is transformed into hydrate of cetyl and a palmitate of the alkali-metal (Smith):

$$C^{32}H^{64}O^2 + KHO = \underset{\substack{\text{Hydrate of}\\ \text{cetyl.}}}{C^{16}H^{34}O} + \underset{\substack{\text{Palmitate of}\\ \text{potassium.}}}{C^{16}H^{31}KO^2}.$$

It must be observed, however, that the statements of different chemists regarding the fatty acids resulting from the saponification of cetin do not quite agree. Chevreul obtained margaric and oleic acid. Heintz (Pogg. Ann. lxxxiv. 232) obtained a mixture of stearic, palmitic, myristic, cocinic, and cetic acids, which he separated by the different solubility of the acids themselves, and of their barium-salts, in alcohol. He therefore regards cetin, not as a simple proximate principle, but as a mixture of the cetyl-salts of the acids just mentioned. By repeatedly crystallising spermaceti from ether, he obtained at last a small quantity of a fatty substance, which melted at 53·5° C., but in other respects exhibited the characters of cetin, and also its composition, viz. 80·03 C, 13·25 H, and 6·72 O.

CETRARIA. See LICHENS.

CETRARIC ACID. *Cetrarin.* $C^{18}H^{16}O^8$. (Berzelius, Schw. J. vii. 317; Ann. Chim. xc. 277.—Herberger, Ann. Ch. Pharm. xxi. 137.—Knop and Schnedermann, *ibid.* lv. 144.)—Contained, together with lichenostearic acid, in Iceland moss (*Cetraria islandica*). To obtain the two acids, the lichen is treated for about a quarter of an hour with a boiling mixture of strong alcohol and carbonate of potassium (15 grm. of the carbonate to each kilogramme of alcohol), whereby the acids are dissolved as potassium-salts. The filtered liquid mixed with hydrochloric acid, deposits the two acids mixed with a green substance; and by treating this mixture with 8 or 10 times its weight of boiling dilute alcohol, the lichenostearic acid is dissolved, while the cetraric acid and the green substance remain undissolved.

To isolate the cetraric acid, which forms the greater part of the residue, this residue is washed several times with a mixture of ether and an essential oil, for the purpose of removing the green matter; it is then boiled with strong alcohol, which dissolves the cetraric acid, and on cooling deposits it in slender needles, which are purified by boiling them with animal charcoal, then dissolving them in potash, and decomposing the potassium-salt with hydrochloric acid. (Knop and Schnedermann.)

Cetraric acid crystallises in extremely fine capillary needles, of dazzling whiteness. It has a pure bitter taste, is nearly insoluble in water, sparingly soluble in ether, very soluble in boiling alcohol. The crystals are anhydrous.

Cetraric acid turns brown when boiled with water; the alcoholic solution also turns brown on boiling: this change is much accelerated by the presence of an alkali. *Sulphuric acid* colours cetraric acid, first yellow, afterwards red: the mass becomes glutinous and dissolves: and water added to the solution throws down ulmic acid. *Hydrochloric acid* dissolves a small quantity of cetraric acid, the undissolved portion assuming a deep blue colour. This blue compound is dissolved with red colour by strong sulphuric acid, and reprecipitated blue by water. This blue precipitate dissolves in a mixture of dichloride and tetrachloride of tin, and alkalis added to the solution throw down a blue lake (Herberger). Cetraric acid is oxidised by *nitric acid*, yielding oxalic acid and a yellow resin. Chlorine and bromine do not appear to act upon it.

Cetraric acid decomposes carbonates, and forms yellow salts, soluble in water and alcohol, and having an intolerably bitter taste. It has a great tendency to form acid salts. The neutral salts cannot be evaporated, even in vacuo, without decomposing and turning brown. The acid salts are precipitated in a gelatinous form, by mixing the neutral salts with half the quantity of hydrochloric acid necessary to saturate the base. They are difficult to wash, but may be evaporated in the air without turning brown.

An alcoholic solution of acid cetrarate of potassium, forms a deep red precipitate with *ferric* chloride, the liquid at the same time assuming a blood-red colour.

Cetrarate of ammonium is obtained as a yellow powder, by treating the acid with gaseous ammonia, of which it absorbs 10·2 per cent. The *lead*-salt, $C^{18}H^{14}Pb^2O^8$, is obtained as a yellow flocculent precipitate, by mixing acetate of lead with cetrarate of ammonium. The *silver*-salt is a yellow precipitate, which rapidly turns brown. (Knop and Schnedermann.)

CETYL. $C^{16}H^{33}$.—A monotomic alcohol-radicle not yet isolated, but supposed to exist in a series of compounds homologous with the ethyl-compounds, and derived from spermaceti. The cetyl-compounds at present known are:

Type H.H.O.

Hydrate of cetyl (cetylic alcohol)	$C^{16}H^{33}.H.O$
Oxide of cetyl (cetylic ether)	$(C^{16}H^{33})^2O$
Oxide of cetyl and sodium	$C^{16}H^{33}.Na.O$
Oxide of cetyl and ethyl	$C^{16}H^{33}.C^2H^5.O$
Oxide of cetyl and amyl	$C^{16}H^{33}.C^5H^{11}.O$
Acetate of cetyl	$C^2H^3O.C^{16}H^{33}.O$
Benzoate of cetyl	$C^7H^5O.C^{16}H^{33}.O$
Butyrate of cetyl	$C^4H^7O.C^{16}H^{33}.O$
Stearate of cetyl	$C^{18}H^{35}.O.C^{16}H^{33}.O$
Succinate of cetyl	$(C^4H^4O^2)''.(C^{16}H^{33})^2.O^2$
Sulphate of cetyl and hydrogen	$(SO^2)''.C^{16}H^{33}.H.O^2$
Sulphydrate of cetyl	$C^{16}H^{33}.H.S$
Sulphide of cetyl	$(C^{16}H^{33})^2S$
Cetyl-xanthic acid	$(CO)''.C^{16}H^{33}.H.S^2$

Type HH.

Bromide of cetyl	$C^{16}H^{33}Br$
Chloride of cetyl	$C^{16}H^{33}Cl$
Iodide of cetyl	$C^{16}H^{33}I$
Cyanide of cetyl	$C^{16}H^{33}Cy$

Type NH³.

Nitride of cetyl, or tricetylamine	$N.(C^{16}H^{33})^3$
Cetylphenylamine	$N\left\{\begin{matrix}C^{16}H^{33}\\C^6H^5\\H\end{matrix}\right.$
Dicetylphenylamine	$N\left\{\begin{matrix}C^{16}H^{33}\\C^{16}H^{33}\\C^6H^5\end{matrix}\right.$

CETYL, ACETATE OF. $C^{18}H^{36}O^2 = C^2H^3O.C^{16}H^{33}.O$, is produced by treating cetylic alcohol with acetic and hydrochloric or sulphuric acid, precipitating by water, dissolving in ether, and evaporating, as an oily liquid, which at a low temperature solidifies, after a while, in a mass of needle-shaped crystals, fusible at 18·5° C. (Becker, Ann. Ch. Pharm. cii. 219.)

CETYL, BENZOATE OF. $C^{23}H^{38}O^2 = C^7H^5O.C^{16}H^{33}.O$.—Obtained by heating chloride of benzoyl with cetylic alcohol in equivalent proportion, dissolving the residue in ether, and precipitating with alcohol. It forms crystalline scales, which melt at 30° C., dissolve readily in ether, and sparingly in alcohol. (Becker, *loc. cit.*)

CETYL, BROMIDE OF. $C^{16}H^{33}Br$.—Produced by the action of bromine and phosphorus on cetylic alcohol. It is a colourless solid body, heavier than water in the melted state, insoluble in water, very soluble in alcohol and ether; melts at 15° C. When distilled, it gives off hydrobromic acid. (Fridau, Ann. Ch. Pharm. lxxxiii. 15.)

CETYL, BUTYRATE OF. $C^{20}H^{40}O^2 = C^4H^7O.C^{16}H^{33}.O$.—Obtained by slowly heating a mixture of cetylic alcohol and butyric acid to 200° C., and proceeding as with the benzoate. It is white, neutral, miscible with ether but not with alcohol, melts more easily than cetylic alcohol, and when cautiously heated in small quantity, volatilises without decomposition. (Handw. d. Chem. 2te Aufl. ii. [2] 929.)

CETYL, CHLORIDE OF. $C^{16}H^{33}Cl$. *Hydrochlorate of Cetene.*—Obtained by the action of pentachloride of phosphorus on cetylic alcohol. The two bodies mixed in fragments in a retort, become heated, melt, and act violently on each other, giving off large quantities of hydrochloric acid. On subsequently distilling the product, oxychloride of phosphorus passes over, and then chloride of cetyl, which may be purified by redistillation with a small quantity of pentachloride of phosphorus, washing with boiling water, and drying in vacuo at about 120° C. If it still contains hydrochloric acid, it must be distilled with lime recently ignited. (Dumas and Péligot, Ann. Ch. Phys. lxxii. 4.)

Chloride of cetyl is a limpid oily liquid of specific gravity 0·8412 at 12° C., insoluble in water and in alcohol, but soluble in ether, whence it may be precipitated by weak alcohol. It distils above 200° C., with partial decomposition, and by prolonged ebullition the whole of the chlorine may be expelled as hydrochloric acid, leaving cetene (p. 838). It is not acted upon by nitric acid, but strong sulphuric acid decomposes it, eliminating hydrochloric acid and forming cetyl-sulphuric acid. It does not absorb ammonia. (Tütscheff, Rép. Chim. pure, ii. 463.)

CETYL, CYANIDE OF. $C^{16}H^{33}.CN$.—Obtained in an impure state, by heating cetylsulphate of potassium with cyanide of potassium, and extracting with ether

(Köhler, Zeitschr. d. gesammt. Naturw. vii. 252; Jahresber. 1856, 579.—Heintz, Pogg. Ann. cii. 257; Jahresber. 1857, 445). According to Köhler, it is a solid crystalline substance, melting at 53° C., easily soluble in ether and in hot alcohol; according to Heintz, it is liquid at ordinary temperatures, but its formation is accompanied by that of a crystalline solid, which melts at 55·1°, and is probably a mixture of cetylic ether with palmitic aldehyde. Heated with potash it appears to yield margaric acid, $C^{17}H^{34}O^2$. (Köhler.)

CETYL, HYDRATE OF. $C^{16}H^{34}O = C^{16}H^{33}.H.O$. *Cetylic Alcohol, Ethal.* (Chevreul, *Recherches sur les Corps gras*, p. 171.—Dumas and Péligot, Ann. Ch. Phys. [2] lxii. 4; Smith, *ibid.* [3] vi. 40; also, Ann. Ch. Pharm. xlii. 247.—Heintz, Pogg. Ann. lxxxiv. 232; lxxxvii. 553.)—This compound is prepared by saponifying spermaceti with an alkali, the cetin, or palmitate of cetyl contained in that substance being then resolved into an alkaline palmitate and hydrate of cetyl, which latter is dissolved out by alcohol or ether. Dumas and Péligot add 1 pt. of solid hydrate of potassium, by small portions and with constant agitation, to 2 pts. of melted spermaceti, treat the resulting soapy mass with water, and then with a slight excess of hydrochloric acid. On boiling the liquid, the ethal and the fatty acids of the soap rise to the surface, in the form of an oily layer, which is separated by decantation, and saponified a second time in the same manner, to decompose a small remaining quantity of spermaceti; the fatty acids are again separated by means of hydrochloric acid, and saponified with slaked lime added in excess. A mixture of lime-soap and hydrate of cetyl is thus obtained, from which the latter is dissolved out by alcohol. Lastly, the alcohol is distilled off, and the cetylic alcohol which remains is purified by crystallisation from ether. Heintz boils spermaceti with an alcoholic solution of potash; precipitates the boiling liquor with a concentrated aqueous solution of chloride of barium; and dissolves out the ethal from the precipitate with alcohol. As the alcohol also dissolves small quantities of barium-salts, it is removed by distillation, and the ethal which remains is dissolved in cold ether, and finally purified by several crystallisations from ether.

Cetylic alcohol or ethal is a white solid crystalline mass, which melts at a temperature above 48° C., but solidifies at 48° (Chevreul). It melts in water at 50° C., and when it solidifies, the temperature rises to 51·5°; when melted alone, it solidifies at 49° or 49·5° (Heintz). When slowly cooled, it crystallises in shining laminæ: it also crystallises on cooling from solution in alcohol. It is without taste or smell, and distils without alteration, passing over even with vapour of water. It is insoluble in water, but mixes in all proportions with alcohol and ether.

Ethal does not give off water when heated with *oxide of lead.* It is not dissolved by *aqueous alkalis;* but when strongly heated with *potash-lime,* it gives off hydrogen, and is converted into a potassium-salt, probably palmitate or ethalate (Dumas and Stas, Ann. Ch. Phys. [2] lxxiii. 124):

$$C^{16}H^{34}O + KHO = C^{16}H^{31}KO^2 + 4H.$$

Ethal is decomposed by *sodium,* yielding *cetylate of sodium,* $C^{16}H^{33}KO$. With *potash* and *sulphide of carbon* it forms cetyl-xanthate of potassium, $C^{16}H^{33}.K.COS^2$. Distilled with *pentachloride of phosphorus,* it forms chloride of cetyl, oxychloride of phosphorus, and hydrochloric acid:

$$C^{16}H^{33}.H.O + PCl^3.Cl^2 = C^{16}H^{33}Cl + PCl^3O + HCl.$$

With *iodine* and *phosphorus,* it yields iodide of cetyl. With strong *sulphuric acid,* it forms cetyl-sulphuric acid, $C^{16}H^{33}.H.SO^4$.

Heintz (*loc. cit.*) regards ethal, not as a simple alcohol, but as a mixture of cetylic and stearic alcohols, $C^{16}H^{34}O$, and $C^{18}H^{38}O$: because, according to his experiments, the *ethalic* acid of Dumas and Stas, is a mixture of palmitic and stearic acids, separable by solution in boiling alcohol and precipitation by acetate of barium.

CETYL, IODIDE OF, $C^{16}H^{33}I$. (Fridau, Ann. Ch. Pharm. lxxxiii. 9).—Prepared by introducing phosphorus into cetylic alcohol heated to 120° C. in an oil-bath, and adding an excess of iodine by small portions at a time, while the mixture is continually stirred. Hydriodic acid is then given off, together with phosphorous acid, while iodide of phosphorus crystallises out, and iodide of cetyl remains in the liquid state. When the reaction is complete, the iodide of cetyl is decanted, washed with cold water, which causes it to solidify, and then crystallised from alcohol. It crystallises in colourless interlaced laminæ, insoluble in water, easily soluble in ether, more soluble in boiling than in cold alcohol. Melts at 22° C., and solidifies on cooling in rosettes having a fatty aspect. Burns with a clear flame, giving off free iodine.

It does not distil without alteration, but decomposes quickly at 250° C., giving off copious vapours of iodine and hydriodic acid, together with an oily hydrocarbon. It is violently attacked by *mercuric* oxide at 200°, yielding an oil (cetene?) together with iodide of mercury and metallic mercury, and leaving a crystallisable solid fusible at 50°. With oxide of silver recently precipitated, and still moist, it forms the same compound, melting at 50°. With cetylate of sodium it yields iodide of sodium and oxide of cetyl·

$$C^{16}H^{33}.K.O + C^{16}H^{33}.I = KI + (C^{16}H^{33})^2O.$$

Ammonia in solution does not act on iodide of cetyl, but gaseous ammonia converts it into tricetylamine, $N(C^{16}H^{33})^3$. With phenylamine it forms cetyl-phenylamine and dicetyl-phenylamine. (Fridau).

CETYL, NITRIDE OF. See CETYLAMINE.

CETYL, OXIDE OF. *Cetylic ether.* $(C^{16}H^{33})^2O$.—Obtained by treating cetylate of sodium, $C^{16}H^{33}KO$, with iodide of cetyl at 110° C., washing the product with boiling water to remove iodide of potassium, and crystallising from alcohol or ether. It crystallises in shining scales. Melts at 55° C., and solidifies between 53° and 54° in a radiated mass; distils at 300° for the most part without decomposition. It is not attacked by hydrochloric or nitro-hydrochloric acid at the boiling heat. but strong sulphuric acid destroys it. (Fridau, Ann. Ch. Pharm. lxxxiii. 20.)

Cetyl-ethyl-oxide or *cetylate of ethyl*, $C^2H^5.C^{16}H^{33}.O$, and *cetyl-amyl-oxide* or *cetylate of amyl*, $C^5H^{11}.C^{16}H^{33}.O$, are obtained in like manner by treating cetylate of sodium with iodide of ethyl or amyl. They both crystallise in laminæ, soluble in alcohol or ether: the ethyl-compound melts at 20° C., the amyl-compound at 30°. (G. Becker, Ann. Ch. Pharm. cii. 220.)

Cetyl-sodium-oxide or *cetylate of sodium*, $C^{16}H^{33}NaO$, obtained by the action of sodium or cetylic alcohol, is a greyish-yellow solid which begins to melt at 100° C. and is perfectly fluid and transparent at 110°. It is not decomposed by boiling water, but hydrochloric acid separates cetylic alcohol from it. (Fridau.)

CETYL, STEARATE OF. $C^{34}H^{68}O^2 = C^{18}H^{35}O.C^{16}H^{33}.O$.—Prepared like the butyrate. Thin white shining laminæ, sparingly soluble in boiling alcohol and in cold ether, easily in boiling ether. Melts at 55°—60° C., and forms a crystalline mass on cooling. Volatilises with partial decomposition when heated in a tube. (Handw.)

CETYL, SUCCINATE OF. $C^{36}H^{70}O^4 = (C^4H^4O^2)''.(C^{16}H^{33})^2.O^2$.—Prepared by heating 1 at. succinic acid with 2 at. cetylic alcohol in an air-bath, neutralising with carbonate of sodium and recrystallising from ether. White laminæ, sparingly soluble in alcohol, more freely in ether-alcohol, still more in pure ether. (Tütscheff, *loc. cit.*)

CETYL, SULPHATE (ACID) OF. *Cetylsulphuric acid. Sulphocetic acid.* $C^{16}H^{34}SO^4 = \left.\begin{matrix}(SO^2)'' \\ C^{16}H^{33}.H\end{matrix}\right\}O^2$.—Produced by mixing sulphuric acid with cetylic alcohol at the temperature of the water-bath (Dumas and Péligot, *loc. cit.*) According to Köhler (*loc. cit.*) and Heintz (*loc. cit.*) the most abundant product is obtained by mixing the two substances at the lowest temperature at which they will act, viz. at the melting point of cetylic alcohol; dissolving the mixture in alcohol and saturating with potash; separating the precipitate from the liquid; concentrating the latter; treating the residue with ether, which extracts undecomposed cetylic alcohol, and leaves cetylsulphate of potassium; and repeatedly crystallising the latter from boiling alcohol.

Cetylsulphate of potassium forms white nacreous laminæ, consisting of interlaced microscopic needles; it is moderately soluble in hot alcohol, less in boiling water, insoluble in ether. It is not fusible. Heated to 140° C. with cyanide of potassium, it yields cyanide of cetyl.

CETYL, SULPHIDE OF. $(C^{16}H^{33})^2S$.—Prepared by the action of chloride of cetyl on an alcoholic solution of monosulphide of potassium at the boiling heat. Chloride of potassium then forms and sulphide of cetyl rises to the surface of the liquid, where it solidifies on cooling. It is then washed with cold water, melted in boiling water, and repeatedly crystallised from a mixture of alcohol and ether, till the melting point becomes fixed at 57·5° C. It forms shining scales resembling those of cetylic mercaptan. It dissolves readily in ether, and in boiling alcohol, very sparingly in cold alcohol. The alcoholic solution forms a white precipitate with acetate of lead, also dissolved in alcohol. (Fridau, Ann. Ch. Pharm. lxxxiii. 16.)

CETYL, SULPHYDRATE OF. *Cetylic Mercaptan.* $C^{16}H^{33}.H.S$.—Prepared by treating sulphydrate of potassium dissolved in alcohol with an alcoholic solution of chloride of cetyl. The product contains a certain quantity of sulphide of cetyl. It is purified by adding acetate of lead, then water, washing with water, and digesting in ether, which dissolves the cetylic mercaptan and deposits it on evaporation in crystalline scales having a silvery lustre. It melts at 50·5°C., but solidifies again only when cooled down below 44°, assuming the form of interlaced dendrites. It is sparingly soluble in cold alcohol, easily in ether, somewhat less easily in boiling alcohol. When boiled with water it gives off a peculiar odour.

The cold alcoholic solution produces, after a while, white flocculent precipitates with the alcoholic solutions of silver-salts and of mercuric chloride; it does not precipitate the salts of lead, platinum or gold. Mercuric oxide does not act sensibly upon it, even at high temperatures. (Fridau, Ann. Ch. Pharm. lxxxiii. 18.)

CETYLAMINES. Bases formed by the substitution of one or more atoms of cetyl in place of hydrogen in a molecule of ammonia. *Mono-* and *di-cetylamine* are not known.

Tricetylamine or *Nitride of Cetyl.* $C^{48}H^{99}N = N(C^{16}H^{33})^3$.—This base is produced by passing ammonia-gas into iodide of cetyl heated to 150° C. A white precipitate of iodide of ammonium is then formed, increasing in quantity if the temperature be maintained for a while at 180°, and the substance which remains in the fused state is tricetylamine. It dissolves in boiling alcohol and crystallises in colourless needles, melts at 39° C. and solidifies in mammellated crystals on cooling.

The salts of tricetylamine are insoluble in water, but soluble in ether and alcohol, especially in the hot liquids. The *hydrochlorate*, $C^{48}H^{99}N.HCl$, crystallises from boiling alcohol in needles, which are less fusible but more soluble than the base itself. Potash added to the boiling solution separates tricetylamine in the form of a heavy oil. The *chloroplatinate*, $C^{48}H^{99}N.HCl.PtCl^2$, is a cream-coloured, almost pulverulent precipitate, insoluble in water, sparingly soluble in alcohol. (Fridau, Ann. Ch. Pharm. lxxxiii. 25.)

Cetylphenylamine, $N.H.C^{16}H^{33}.C^6H^5$, and *Dicetylphenylamine*, $N.(C^{16}H^{33})^2.C^6H^5$, are produced by the action of iodide of cetyl on phenylamine (*q. v.*)

CETYL-XANTHIC ACID. $C^{17}H^{34}OS^2 = \left.\begin{matrix}(CO)''\\ C^{16}H^{33}.H\end{matrix}\right\}S^2$.—This acid is known only as a potassium-salt, which is prepared by adding alcohol and hydrate of potassium to a saturated solution of cetylic alcohol in sulphide of carbon, heating the mixture a little below the boiling point of alcohol, then leaving it to itself for a while and decanting. The clear solution, on cooling, deposits light scales, which may be purified by washing with a small quantity of cold alcohol and dissolving in boiling alcohol.

The salt is white, tasteless, odourless, very hygroscopic and unstable. Its alcoholic solution gives a white precipitate with *mercuric chloride*; canary-yellow with nitrate of *silver*, blackening in a few minutes; white with acetate of *lead*, also blackening rapidly; white gelatinous with salts of *zinc*. Digested with hydrochloric acid, it yields cetylic alcohol. (Desains and De La Provostaye, Ann. Ch. Phys. [3] vi. 494.)

CEVADIC ACID. An acid existing in the seed of sabadilla (*Veratrum Sabadilla*, Ritz), and probably also in the root of white hellebore (*Veratrum album*), and of *Colchicum autumnale.* To prepare it, the oil extracted from sabadilla seeds by ether is saponified with potash; the soap decomposed by tartaric acid; the mixture distilled; the distillate neutralised with baryta; and the resulting barium-salt evaporated to dryness, and distilled with syrupy phosphoric acid. Cevadic acid then sublimes in white nacreous needles. It is soluble in water, alchohol, and ether, and smells like butyric acid; melts at 20° C. and sublimes at a temperature a few degrees higher. Its salts have a peculiar odour. The ammonium-salt gives a white precipitate with ferric salts.

CEVADIN or **HORDEIN.** A mixture of starch, cellulose, and azotised matter obtained from barley.

CEYLANITE or **CEYLONITE.** A ferruginous variety of spinel (Al^2MgO^2), from Ceylon, and other localities, having the magnesium more or less replaced by ferrosum, and the aluminium by ferricum. It is the *pleonast* of Haüy. (See SPINEL.)

CHABASITE. A mineral belonging to the zeolite family, and consisting essentially of hydrated silicate of aluminium and calcium, a certain portion of the calcium being however always replaced by potassium or sodium. It crystallises in forms belonging to the hexagonal system. Primary form, an obtuse rhombohedron, having the angle of the terminal edges = 94° 46′. It occurs in the primary form, and in the combination $R . -\frac{1}{2}R . -2R$. Ratio of principal to secondary axes = 1·086. Cleavage distinct parallel to R. Specific gravity 2·0 to 2·1. Hardness 4—4·5. Transparent and colourless, sometimes flesh-red, with vitreous lustre. Streak uncoloured. Fracture uneven. Brittle. Shrinks before the blowpipe to a blistered, slightly translucent enamel. It is perfectly decomposed when heated in the state of powder before the blowpipe. It occurs in scattered crystals in the fissures of some trap rocks, and in the hollows of certain geodes disseminated in the same rocks.

The composition of most varieties of chabasite is nearly represented by the formula $Ca^2O.Al^4O^3.4SiO^2 + 6aq.$, which (if $al = \frac{2}{3}$ Al), may be reduced to that of a metasilicate $(Ca\ al^2)Si^2O^6 + 3aq$. Sometimes, however, the amount of alkali is considerable, as in the fourth of the following examples, which approaches nearly to $\left.\begin{matrix}Ca^{\frac{1}{2}}\\Na^{\frac{1}{2}}\end{matrix}\right\}al^3Si^2O^6 + 3aq.$

Analysis *a* is of a specimen from Kilmalcolm in Renfrewshire, by Thomson; *b*, from Aussig in Bohemia, by Rammelsberg; *c*, from Annerode near Giessen, by Genth; *d*, from Port Rush in Ireland, by Thomson:

	SiO^2	Al^4O^3	Fe^4O^3	Ca^2O	Na^2O	K^2O	H^2O	
a . .	48·75	17·44	—	10·47	—	1·45	21·72	= 99·93
b . .	47·91	18·14	—	9·64	0·25	2·56	21·50	= 100·00
c . .	47·00	19·71	0·15	10·63	0·65	0·33	22·29	= 100·76
d . .	48·99	19·77	0·40	4·07	6·07	—	20·70	= 100·00

Sometimes, however, the proportion of silica is somewhat greater, and the composition is more nearly represented by the formula $2(Ca^2O.Al^4O^3).5SiO^2 + 12aq.$ or $(Ca^4al^{12}H^2)Si^9O^{27} + 11aq.$; and here again, the proportion of alkali-metal may be considerable, as in the variety called *acadiolite*, which may be represented by the formula $(Ca^{\frac{2}{5}}Na^{\frac{2}{5}}K^{\frac{1}{5}})^4al^{12}H^2Si^9O^{27} + 11aq.$ Analysis *e* is chabasite from Drottning Grufva near Gustassberg in Jemtland (Berzelius); *f* is *acadiolite*, from New Caledonia (Hayes):

	SiO^2	Al^4O^3	Ca^2O	Na^2O	K^2O	H^2O	
e . .	50·65	17·90	9·37	—	1·70	19·90	= 99·52
f . .	52·02	17·88	4·24	4·07	3·03	18·30	= 99·54

(*Rammelsberg's Mineralchemie*, p. 816.)

According to Dana, *Haydenite* from Jones' Falls in Maryland, is merely a ferruginous variety of chabasite crystallised in scalenohedrons.—*Phacolite* from Leipa in Bohemia is another mineral of similar constitution, but containing less water, viz. $(M^4al^{12}H^2)Si^9O^{27} + 9aq.$

CHÆROPHYLLUM. The fleshy root of *Chærophyllum bulbosum*, which is now coming into use in France as an article of food, has been examined by Payen (Compt. rend. xliii. 269), and compared with that of the potato (a yellow variety):

	Chærophyllum.	Potato.
Water	63·618 . . .	74·00
Starch, &c.	28·634 . . .	21·20
Cane-sugar	1·200	
Albumen and other nitrogenous substances .	2·600 . . .	1·50
Fat	0·348 . . .	0·10
Inorganic matters	1·500 . . .	1·56
Cellulose and pectin-substances	2·100 . . .	1·64

The comparison is evidently to the advantage of the chærophyllum. According to Polstorf (N. Arch. Pharm. v. Brandes, xviii. 176), the seeds of this plant contain an alkaloïd, *chærophylline*. Most species of chærophyllum are aromatic.

CHAILLETIA TOXICARIA. An ulmaceous plant possessing poisonous seeds.

CHALCANTHITE. Native sulphate of copper. (See SULPHATES.)

CHALCEDONY or *Calcedony*.—A variety of quartz exhibiting various shades of white, yellow, grey, brown, green, and blue. It has usually the subdued lustre of wax, and is transparent or translucent, some milk-white varieties being opaque. It occurs in mammillary and botryoïdal shapes, and as stalactites in cavities roofed or lined with it. According to Fuchs, it is true quartz with some opal disseminated through it. Varieties of chalcedony are: agate, carnelian, cat's eye, chrysoprase, flint, hornstone, onyx, plasma, and sand (*q. v.*) Common chalcedony occurs in the toadstone of Derbyshire, in the trap rocks of Fifeshire, the Pentland Hills, and the Hebrides; magnificent specimens also in Trevascus Mine in Cornwall, in Iceland, and in the Faroe Isles.

CHALCODITE. A hydrated magnesio-ferrous silicate found near Antwerp in Jefferson county, New York, and originally mistaken for cacoxene. It occurs in stellate globular masses, having a bronze-like aspect, or as a deposit upon red hæmatite; also in prisms with very distinct cleavage in one direction. Translucent, yellowish-brown to blackish-green, with somewhat lighter streak. Lustre metalloïdal; on the cleavage faces, metallic and nacreous. Very flexible in thin laminæ. Hardness 1 to 1·5. Before the blowpipe, it gives off water, and exhibits the reactions of iron. Hydrochloric acid does not act upon it in the cold, but when heated, decomposes it with separation of silica. (C. U. Shepard, Sill. Am. J. [2] xiv. 265.)

CHALCOLITE. See URANITE.

CHALCOPHACITE. Octahedral arsenate of copper. (See LIROCONITE.)

CHALCOPHYLLITE. Syn. with COPPER-MICA.

CHALCOPYRITE. Syn. with COPPER-PYRITES.

CHALCOSTIBITE. Native sulphantimonite of copper. (See WOLFSBERGITE.)

CHALCOTRICHITE. Native cuprous oxide. (See COPPER, OXIDES OF.)

CHALILITE. This name is applied to two minerals found imbedded in grey almond-stone, from the county of Antrim in Ireland. One of these minerals is amorphous, with conchöidal fracture; cream-coloured, with faint waxy lustre; translucent on the edges, with faint lustre on the streak; slightly unctuous to the touch, and adhering to the tongue. In water, it falls to pieces with decrepitating noise. It is decomposed by hydrochloric acid, with separation of pulverulent silica.

According to v. Hauer (Wien Acad. Ber. xii. 229) it contains

SiO^2	Al^4O^3	Fe^2O	Ca^2O	Mg^2O	H^2O		Total.
44·11	10·90	1·05	6·74	13·01	24·07	=	99·88

with traces of manganese and potassium, whence the formula: $4M^2O.Al^4O^3.6SiO^2 + 13H^2O$.

The other mineral (first analysed by Thomson), is a dense aggregate of concentrically fibrous spherules, of pale blood-red colour; glistening; translucent on the edges; of hardness 5, and specific gravity 2·24. It does not fall to pieces in water, and when decomposed by hydrochloric acid, yields a jelly of silica.

This mineral, analysed by v. Hauer (Wien Acad. Ber. xi. 18) gave:

SiO^2	Al^4O^3	Fe^4O^3	Ca^2O	Mg^2O	Loss by ignition.		Total.
38·26	27·71	trace	12·01	6·85	14·32	=	99·15

whence the formula $6M^2O.4Al^4O^3.9SiO^2 + 12H^2O$ (Kenngott, Jahresber d. Chem. vi. 826; vii. 842). Both minerals are orthosilicates, the formula of the first being reducible to $(M^8al^6H^{10})Si^6O^{24} + 7aq.$ which is of the form $6R^4SiO^4 + 7aq.$, and that of the second to $(M^4al^8)Si^3O^{12} + 4aq.$ or $3R^4SiO^4 + 4aq.$

CHALK. Friable carbonate of calcium, very abundant, and forming the upper member of the cretaceous group which occupies nearly the whole of the south-eastern part of England, and a considerable portion of the north of France. It is white and opaque, very soft, and without the least appearance of polish in its fracture. Specific gravity 2·4 to 2·6. It contains about 2 per cent. of clay, besides free silica. Some specimens, perhaps most, contain a little iron. Sometimes also magnesia and chloride of calcium occur in small quantities. It may be purified by trituration and elutriation, the ferruginous and siliceous particles subsiding first, while the pure chalk particles remain suspended: this purified chalk when dried is called *whiting*. Chalk is extensively used in agriculture, as an addition to soils which are deficient in lime.

The name *chalk* is also occasionally applied to other earthy minerals; thus *Black chalk* is a peculiar kind of slate, also called *Drawing slate*, which produces a black shining streak on paper, and is used in crayon drawing. *Red chalk* is a clay, coloured by oxide of iron.

CHALK STONES. Gouty concretions in the joints, so called from their resemblance to chalk. They consist mainly of uric acid.

CHALKOSINE. Syn. with COPPER-GLANCE.

CHALYBEATE WATERS. Mineral waters containing carbonate of iron dissolved in excess of carbonic acid (p. 785).

CHALYBITE. Native carbonate of iron (p. 784).

CHAMÆLEON MINERAL. Manganate of potassium. (See MANGANATES.)

CHAMÆROPS HUMILIS. The leaves of this palm are coated with wax, separable by alcohol into cerin and myricin. (Teschemacher, *Rochleder's Phytochemie*, p. 219.)

CHAMOISITE. A black earthy mineral from Chamoisin in the Valais, containing, according to Berthier (Ann. Min. v. 393), 14·3 per cent. silica, 60·5 ferrous oxide, 7·8 alumina, and 17·4 water (=100), with 15 per cent. of carbonate of calcium. It is perhaps a mixture of magnetic iron ore with a hydrated silicate of aluminium.

CHAMOTTE. A mixture of fire-clay and fragments of burnt pottery used for making fire-bricks, pipes, crucibles, &c. *Chamotte-stones* from the kaolin of Halle, were found by Wackenroder (Arch. Pharm. [2] lxxv. 27), to contain 85·00 per cent. silica, 11·33 alumina, 2·23 ferric oxide, and a trace of magnesia; loss by ignition 1·00.

CHAMPAGNE WINE is made from selected grapes, red and white, the must of which, after fermenting in the vats from 12 to 15 hours, is drawn clear off into the casks; it is racked off about Christmas, once more after four weeks, and then fined with isinglass, which treatment is also repeated. The new wine is put into stout bottles in the month of May, leaving about 2 inches empty under the corks, which are wired down; and the bottles are laid on their sides for the progress of the fermentation: from 6 to 10 per cent. of the bottles burst. This stage of the process is completed in September, when the bottles are placed on their mouths, and left so for fourteen days to let the sediment settle in the neck, which settlement is promoted by a slight shaking. By dexterous opening of the bottles, the muddy deposit is discharged, and they are then filled up with clear wine, corked afresh, and packed up for transport, the cork being covered either with melted resin, wax, or tin-foil. In seasons or districts when the must is not sweet enough, sugar is added by pouring a thimble-full of syrup (called *liquor*), into each bottle, the wine destined for Russia receiving a double dose.

A like procedure is followed in making the sparkling wines of Germany, as on the Moselle, and at Esslingen in Wurtemburg. Carbonic acid gas is frequently condensed by an air-pump into the other more or less factitious frothing wines of France and Germany. U.

CHANTONITE. A mineral said to exist in certain meteorites (*q.v.*)

CHARA FŒTIDA. The ash of this plant has been analysed by Schulz-Fleeth (Pogg. Ann. lxxxiv. 80). Two specimens of the dried plant yielded 54·58 and 68·39 per cent. of ash, the chief characteristic of which was the very large quantity of lime which it contained, viz. 42·7 per cent., which exists in it almost entirely in the form of carbonate. The water in which the plant grew yielded in 100 pts. 0·1618 pt. of solid matter, of which 0·104 consisted of carbonate of calcium.

CHARCOAL. See Carbon (p. 759); also *Ure's Dictionary of Arts, Manufactures and Mines*, i. 615).

CHATHAMITE. Native arsenide of cobalt. (See Cobalt.)

CHAVICA OFFICINARUM. One of the names of the plant which yields *long pepper*. (See Pepper.)

CHAY or **CHAYA ROOT.** The root of the *Oldenlandia umbellata*, which grows wild on the coast of Coromandel, and is likewise cultivated there for the use of dyers and calico-printers. It is used for the same purposes as madder, to which it is said to be far superior, giving the beautiful red so much admired in the Madras cottons. U.

CHEESE is formed from milk by coagulating it with rennet; separating the curd from the whey; compressing the curd in moulds, after it is duly seasoned with salt; and keeping this solidified milk in a cool place for some time, to allow it to undergo a kind of fermentation, by which it acquires the flavour and other well known properties of cheese. The chemical changes undergone by the casein in this process are little understood. The milk, before it is coagulated, should be heated to about 85° F.; then it receives the rennet—the infusion in water of the stomach of a new-born calf, commonly salted and dried to make it keep. The rennet effects its curdling completely in about an hour and a half. The curd is cut with a three-bladed knife; drained of its whey; broken down by hand or otherwise, subjected to compression; then comminuted more completely; put into its mould; and exposed to a graduated pressure, commonly under a heavy weight, but in large dairies by a screw press, which can be progressively tightened. The comminuted curd may be well salted by enclosing it in linen cloth and immersing it for one day or several days in brine. It is then drained, wiped, and set away in a cold room. Roquefort cheese is made from a mixture of sheep and goats' milk, and is ripened in a chamber or cellar having a very low temperature. U.

The following table exhibits the composition of several kinds of cheese, as determined by Payen (J. Pharm. [3] xvi. 279).

Composition of Cheese.

	Water in 100 pts.	Ash in 100 pts. of substance:		Nitrogen in 100 pts. of substance:			Fat in 100 pts. of substance.	
		normal.	dry.	normal.	dry.	ash-free	normal.	dry.
Cheese from Chester	30·89	4·78	6·88	5·56	8·00	8·59	25·41	36·61
„ Brie	53·99	5·63	12·08	2·39	5·14	5·85	24·83	33·29
„ Neufchatel	61·87	4·25	11·17	2·28	5·99	6·07	18·74	49·15
„ Marolles	40·07	5·93	9·91	3·73	9·24	6·92	28·73	47·95
„ Roquefort	26·53	4·45	6·06	5·07	6·91	7·35	32·31	43·98
„ Holland	41·41	6·21	10·61	4·10	7·01	7·84	25·06	42·78
„ Gruyères	32·05	4·79	7·05	5·40	7·96	8·59	28·40	41·81
„ Parmesano	30·31	7·09	10·16	5·48	7·87	8·76	21·68	31·12

The *ash* of two samples of cheese has been analysed by Johnson (Ann. Ch. Pharm. lxxviii. 119): *a*. Hand-cheese (*Hand-Käse*) from the neighbourhood of Giessen, *b*. Swiss cheese.

K^2O	Na^2O	Ca^2O	Mg^2O	Fe^4O^3	CO^2	P^2O^5	NaCl
4·85	7·33	2·55	—	0·11	0·03	13·68	72·47 = 101·02
2·46	3·67	17·82	0·81	0·17	0·08	20·45	55·37 = 100·83

The hand-cheese exhibited an alkaline reaction; gave off 46·35 per cent. water at 100° C; the dried substance yielded 12·86 per cent. nitrogen and 13·15 per cent. ash. The Swiss cheese yielded 44·70 per cent. water, and, after drying, 8·0 per cent. nitrogen and 11·36 per cent. ash.

On the preparation of cheese, see *Traité de Chimie générale, par Pelouze et Frémy*, 2me éd. vi. 213, and *Muspratt's Chemistry*, article CHEESE.

CHEIRANTHUS CHEIRI. *Wallflower.*—The fragrant flowers of this plant have a bitter taste like that of cress. They contain a substance which assumes a carmine colour in contact with sulphuric acid. The seeds contain myrosin, but no myronic acid. (*Rochleder's Phytochemie*, p. 98.)

CHELERYTHRINE. An alkaloïd existing in very small quantity in *Chelidonium majus* (Probst, Ann. Ch. Pharm. xxix. 120; xxxi. 250). It forms orange-red salts, and, according to Schiel (Sill. Am. J. [2] xx. 220), is identical with sanguinarine, $C^{19}H^{16}O^4$, the alkaloïd of *Sanguinaria canadensis*. (See SANGUINARINE.)

CHELIDONIC ACID. $C^7H^4O^6 = \left.\begin{matrix}C^7HO^3\\H^3\end{matrix}\right\}O^3$. (Probst. Ann. Ch. Pharm. xxix. 116.—Lerch, *ibid.* lvii. 273.—Hutstein, N. Br. Arch. lxv. 23.—Gm. xiv. 413.—Gerh. iii. 754).—This acid exists in all parts of *Chelidonium majus*, the common celandine, in the form of a calcium-salt, together with malic acid and another acid, probably fumaric: it is most abundant at the flowering time. To obtain it, the expressed juice is coagulated by heat and filtered. The filtrate is acidulated with nitric acid, and nitrate of lead is added in small quantities, as long as a crystalline precipitate falls, care being taken not to add too much either of the acid or of the lead-salt. The precipitate, which contains lime, is diffused in a large quantity of water and decomposed by sulphuretted hydrogen, which takes place slowly; the solution of acid chelidonate of calcium is neutralised with chalk and boiled with animal charcoal; and the neutral liquid is evaporated till saline crusts form. After cooling, white crystals are obtained, of a silky lustre, which are to be purified by repeated crystallisation. To separate the acid, the chelidonate of calcium thus obtained is dissolved in water, the solution precipitated with carbonate of ammonia, and the concentrated solution of chelidonate of ammonium mixed with twice its volume of moderately dilute hydrochloric acid. Chelidonic acid is then precipitated as a mass of crystalline needles, which are to be drained on a filter, washed, and purified by crystallisation from hot water.

Chelidonic acid thus prepared contains 2 at. water of crystallisation, $C^7H^4O^6.2H^2O$, which it gives off (amounting to 9·2 per cent.) at 100° C., or when left over oil of vitriol. By spontaneous evaporation it may be obtained in long needles containing 3 at. water (12·7 per cent.). It dissolves sparingly in cold, more freely in boiling water, the solution solidifying as it cools. According to Probst, it requires for solution 166 pts. of water at 6° C. and 26 pts. at 100°. It dissolves in hydrochloric and sulphuric acids more abundantly than in water, and in 700 pts. of 75 per cent. alcohol at 12° C.

The acid dried at 100° C. gives off 2·0 per cent. ($\frac{1}{2}$ at.) water at 150°, probably with partial decomposition. If the heat be continued, no further loss takes place short of 210°; but at that temperature the acid sustains a considerable though not determinable loss; between 220° and 225° decomposition takes place, the residue becoming soft, blackening, and giving off carbonic anhydride. The black mass, treated with water, yields an acid which crystallises in yellowish crusts. Chelidonic acid burns with slight detonation when heated in the air. It is scarcely attacked by strong nitric acid: but moderately dilute nitric converts it, with evolution of nitric oxide and carbonic anhydride, into another acid; malic acid does not appear to be formed. Chelidonic acid dissolves without decomposition in cold oil of vitriol; but on the application of heat, the solution becomes yellowish, and gives off gas-bubbles, assumes a fine purple-red colour at the boiling heat, but after long boiling, gives off sulphurous acid and acquires a dull undefinable colour. When the calcium-salt is boiled with potash, oxalic acid is produced. (Lerch.)

CHELIDONATES.—Chelidonic acid is a strong acid, dissolving zinc and iron, with evolution of hydrogen, and decomposing carbonates. It is tribasic, its salts being *trimetallic*, $C^7HM^3O^6$, *dimetallic*, $C^7H^2M^2O^6$, or *monometallic*, $C^7H^3MO^6$, besides a few acid salts containing $C^7H^3MO^6.C^7H^4O^6$.

The *dimetallic* chelidonates are formed when the acid is neutralised with a metallic oxide or a carbonate; with alkalis or their carbonates, trimetallic salts are apt to form. Most of the dimetallic salts are soluble in water and crystallisable; they contain several atoms of water, which are given off at or above 150° C.; the ammonium- and silver-salts, however, become anhydrous at 100°. Those which contain colourless bases are themselves colourless. They have no action upon litmus. The *monometallic* salts are produced by heating the dimetallic salts with about ⅓ of their weight of free chelidonic acid or a dilute mineral acid. If the acid is in excess, acid salts are produced. The monometallic salts are resolved by repeated recrystallisation into acid and dimetallic salts. The *trimetallic* salts are formed by treating the dimetallic salts with a caustic alkali or alkaline carbonate. Those which contain colourless bases have a fine lemon-yellow colour; those which are soluble impart a deep colour to the water. Most of them contain several atoms of water, which are not given off at 100° C. They have no reaction upon litmus. They are decomposed by continued contact with water; those of the alkali-metals absorb carbonic acid from the air and yield a dimetallic chelidonate and a carbonate.

The *acid* chelidonates crystallise from the solutions of the dimetallic salts in hot hydrochloric acid, in delicate needles or scales, which do not give off their water of crystallisation at 100° C. They redden litmus, and may be recrystallised, but give up their base when repeatedly treated with hydrochloric acid.

Chelidonate of Ammonium. $C^7H^2(NH^4)^2O^6$.—A boiling dilute solution of the dicalcic salt neutralised with carbonate of ammonium, filtered and evaporated, yields the ammonium-salt, on cooling, in snow-white silky needles. The solution abandoned to spontaneous evaporation, ultimately solidifies to a transparent mass, which when collected and drained on a filter, yields the ammonium-salt in long capillary crystals resembling a knot of the finest silver-white hair. It effloresces in contact with the air, gives off 14·23 per cent. (2 at.) water at 100° C., and then exactly resembles sulphate of quinine. (Lerch.) It does not give off ammonia, either when exposed to the air at ordinary temperatures, or when heated to 100°. Heated above 160°, it turns brownish and gives off carbonate off ammonium; the residue does not contain any other acid. By repeatedly evaporating the solution and redissolving the residue, it is converted into the acid salt. It does not form a trimetallic salt when treated with carbonate of ammonium or caustic ammonia. (Lerch.)

Chelidonates of Barium.—The *tribarytic salt*, $C^7HBa^3O^6 + 3aq.$ (at 100°), is obtained by mixing a hot solution of the dibarytic salt with ammonia, precipitating with chloride of barium, and quickly washing the precipitate with water. It is a lemon-yellow powder which does not give off water at 100° C. It absorbs carbonic acid from the air, dissolves sparingly in water, not at all in alcohol.

The *dibarytic salt*, $C^7H^2Ba^2O^6 + aq.$, is obtained by decomposing the corresponding calcium-salt with a soluble barium-salt, or by neutralising the aqueous acid with baryta or its carbonate. It is colourless, crystalline, and very brittle; soluble in water.

The *acid salt*, $C^7H^3BaO^6.C^7H^4O^6 + 2aq.$ is produced by dissolving the tribarytic salt in boiling hydrochloric acid.

Chelidonates of Calcium.—The *tricalcic salt*, $C^7HCa^3O^6 + 3aq.$ (at 100° C.) is prepared by boiling the dicalcic salt with ammonia, or by decomposing the sodium-salt mixed with ammonia with chloride of calcium. It is a yellow amorphous powder, very little soluble in water, insoluble in alcohol.

The *dicalcic salt*, $C^7H^2Ca^2O^6 + 3aq.$ (at 100°), occurs in *Chelidonium majus* (p. 847). It crystallises in silky prismatic needles, very little soluble in cold water, but easily in boiling water; insoluble in absolute alcohol. The solution does not affect litmus. The salt is not efflorescent, and does not part with its water of crystallisation below 150° C.

The *acid salt*, $C^7H^3CaO^6.C^7H^4O^6 + 2aq.$, obtained by decomposing the preceding with hydrochloric acid, crystallises in needles.

Chelidonate of Copper.—Green sparingly soluble prisms, obtained by evaporating a mixture of an alkaline chelidonate with sulphate of copper.

Chelidonates of Iron.—The aqueous acid dissolves iron, forming *ferrous chelidonate.*

Ferric Chelidonate.—$Fe^4O^3.C^{14}H^4O^{10} = 2C^7H\mathit{fe}^3O^6 + H^2O$.—The solution of iron in chelidonic acid passes to a higher degree of oxidation during evaporation, and deposits a dingy yellow precipitate. The disodic salt forms with aqueous sesquichloride of iron, a dingy yellow precipitate, somewhat soluble in acetic acid and in excess of sesquichloride of iron; it does not diminish in weight at 100° C., and if set on fire at one point, burns away with a sparkling light, leaving charcoal and sesquioxide of iron. (Lerch.)

When chelidonate of potassium is mixed with excess of sesquichloride of iron, the greater part of the ferric chelidonate remains dissolved; the pale yellow filtrate gradually assumes a darker colour, and ultimately becomes black-brown and opaque, but recovers its pale yellow colour after some time; on heating the liquid, the changes of colour take place more quickly. The dark brown liquid forms with ammonia a rusty brown precipitate, which becomes black when treated with a larger quantity of ammonia, probably from formation of protoxide of iron.

Chelidonates of Lead.—A *basic salt*, $2C^7HPb^3O^6.3Pb^2O$, is obtained by adding the diplumbic salt mixed with ammonia to basic acetate of lead.

The *triplumbic salt*, $C^7HPb^3O^6$, is produced by treating the diplumbic salt with ammonia, or by mixing a cold solution of dicalcic chelidonate with basic acetate of lead. Yellowish-white flakes are then deposited containing $\frac{3}{2}$ at. water ($2C^7HPb^3O^6.3H^2O$), which is given off between 150° and 160° C., the salt then turning yellow. If the solutions are mixed at the boiling heat, the anhydrous salt is produced at once in the form of a lemon-yellow precipitate, darker in colour if mixed with the preceding. It is decolorised and decomposed by acids. Insoluble in water and in alcohol, soluble in lead-salts.

The *diplumbic salt*, $C^7H^2Pb^2O^6 + aq.$, is deposited, on mixing the dicalcic salt with nitrate of lead, in small shining crystalline scales or slender needles, which are insoluble in water, soluble in lead-salts and in ordinary strong nitric acid, but not in fuming nitric acid.

Chelidonate of Magnesium.—Efflorescent needles, obtained by neutralising the hot aqueous acid with carbonate of magnesium.

Chelidonates of Potassium.—The *tripotassic salt* is deposited in yellow crystals from a solution of the dipotassic salt mixed with caustic potash. It has no alkaline reaction when pure, but absorbs carbonic acid from the air, and is converted into the colourless dipotassic salt. Boiled with excess of caustic potash, it yields oxalate of potassium.

The *dipotassic salt* is obtained by decomposing the dicalcic salt with carbonate of potassium.

A *chelidonate of calcium and potassium*, $C^7HKCa^2O^6$, is obtained by mixing a concentrated solution of the dicalcic salt with an equivalent quantity of carbonate of potassium. In a very dilute solution, the lime is immediately precipitated as carbonate.

Chelidonates of Silver.—The *triargentic salt*, $C^7HAg^3O^6$, is obtained by precipitating the tricalcic or the dicalcic salt, mixed with ammonia, with nitrate of silver. It is a yellow very unstable precipitate.

The *diargentic salt*, $C^7H^2Ag^2O^6$, is produced by dissolving oxide of silver in chelidonic acid, or by precipitating the dicalcic salt with nitrate of silver and heating to the boiling point. It then separates on cooling in long colourless needles resembling acetate of silver. It is permanent in the air at ordinary temperatures, and is not altered between 100° and 200° C.; decomposes with slight detonation between 140° and 150°. It dissolves in water, ammonia, and strong nitric acid, but not in alcohol.

Chelidonate of silver and calcium, $C^7HCaAg^2O^6$, is obtained by mixing a concentrated ammoniacal solution of the dicalcic salt with a concentrated solution of nitrate of silver, as a light yellow precipitate, which alters but little in drying, and is decomposed by water only after long continued boiling.

Chelidonates of Sodium.—The *trisodic salt* has not been obtained in definite form.

The *disodic salt*, $C^7H^2Na^2O^6 + 4aq.$, is prepared by decomposing the dicalcic salt with carbonate of sodium; care must be taken not to add too large an excess of the latter, which would give rise to the simultaneous formation of trisodic chelidonate, and a trimetallic salt containing both calcium and sodium, a reaction which is immediately indicated by the yellow colouring of the liquid.

The disodic salt is very soluble in water both hot and cold, and is difficult to crystallise. By slow evaporation, however, small prismatic needles are obtained, which effloresce slowly when exposed to air. They contain 21·16 per cent. water of crystallisation, of which 15·5 per cent. goes off, at 100° C., the rest between 150° and 160°.

The *monosodic salt*, $C^7H^3NaO^6 + 2aq.$, is obtained in slender needles by treating the disodic salt with chelidonic acid.

The disodic salt treated with boiling hydrochloric acid, yields slender needles or scales, which appear to consist of an *acid salt*, $C^7H^3NaO^6.C^7H^4O^6 + 3aq.$

Chelidonate of Strontium.—Slender needles obtained by dissolving the carbonate in chelidonic acid.

Chelidonate of Zinc.—Obtained by saturating the acid with oxide of zinc; it is crystalline, and has an acid reaction.

CHELIDONINE. $C^{20}H^{19}N^3O^3$ (?) (Godefroy, J. Pharm. Dec. 1824; Probst, Ann. Ch. Pharm. xxix. 123; Realing, *ibid.* 131; Will, *ibid.* xxxv. 113; Gerh. iv. 210.)—An alkaloïd contained in all parts of the *Chelidonium majus*, especially in the root. It is obtained by exhausting the root with water acidulated with sulphuric acid, precipitating by ammonia, dissolving the precipitate in alcohol acidulated with sulphuric acid, reprecipitating by ammonia, and treating the residue with ether, which dissolves chelerythrine (sanguinarine) and leaves chelidonine. To purify this product, it is dissolved in the smallest possible quantity of water acidulated with sulphuric acid; the solution is mixed with twice its volume of strong hydrochloric acid, which, after a while, throws down a granular precipitate of hydrochlorate of chelidonine; the precipitate is digested with ammoniacal water, which sets the chelidonine at liberty; and the base thus obtained is crystallised from strong alcohol — or better from acetic acid.

Chelidonine crystallises in small colourless tablets, insoluble in water, soluble in alcohol and ether. It melts at 130° C. to a colourless oil, and decomposes at a higher temperature. The crystals contain 2 at. crystallisation-water, which escapes entirely at 100° C. According to Will's analyses, the base dried at 100° contains 67·4 to 68·1 per cent. C, 5·6 hydrogen, and 12·2 nitrogen; the formula $C^{20}H^{19}N^3O^3$ requires 68·8 C, 5·4 H, 12·1 N, and 13·7 O. Water of crystallisation, by analysis, 46·5 to 5·13; by calculation 4·91.

Chelidonine dissolves readily in acids, forming salts which have a bitter taste and redden litmus. Its compounds with the weaker acids, such as the acetate, are decomposed by evaporation. Ammonia added to solutions of the salts throws down a bulky curdy precipitate, which after a while contracts into a granular crystalline mass. The salts are likewise precipitated by tincture of galls.

According to Probst, solutions of chelidonine are not poisonous.

Hydrochlorate of chelidonine is crystallisable, and dissolves in 325 pts. of water at 18° C. The *chloroplatinate*, $C^{20}H^{19}N^3O^3.HCl.PtCl^2$, is a flocculent, afterwards granular precipitate, yielding by analysis 17·42 and 17·60 per cent. platinum, the formula requiring 17·77.

The *nitrate* is sparingly soluble in water; the *sulphate* and *phosphate* are very soluble both in water and in alcohol: all three salts are crystallisable.

The *acetate* is obtained by decomposing the sulphate with acetate of barium: it is very soluble in water and alcohol, and dries up to a gummy mass.

CHELIDONINIC ACID. $C^7H^{10}O^6$? (Zwenger, Ann. Ch. Pharm. cxiv. 350). —This is another acid contained in very small quantity in *Chelidonium majus*. When the decoction of the plant acidulated with acetic acid, is treated with neutral acetate [or nitrate] of lead, chelidonic acid is precipitated, and chelidoninic acid remains in solution; and by treating the filtrate with basic acetate of lead, not in excess, decomposing the precipitate with sulphuretted hydrogen, evaporating the filtrate, extracting with ether, and again evaporating, chelidoninic acid is obtained in hard, mammellated, yellow crystals. It dissolves easily in water, alcohol, and ether, and separates from the aqueous solution in hard, white, anhydrous crystals, having the form of an oblique rhomboïdal prism. It has a strongly acid taste, decomposes carbonates, and dissolves iron, with evolution of hydrogen. It melts at 195° C.; its vapour is extremely irritating. With *nitrate of silver*, it forms a white, crystalline, sparingly soluble precipitate. *Nitric acid* converts the acid into oxalic acid. Zwenger assigns to crystallised chelidoninic acid the formula $C^{14}H^{11}O^{13}$; it may perhaps be $C^{14}H^{10}O^{12}.HO$, or $2C^7H^{10}O^6.H^2O$.

CHELIDOXANTHIN. A yellow bitter substance contained in the root, leaves, and flowers of *Chelidonium majus*. It is obtained by precipitating the juice with subacetate of lead, decomposing the precipitate with sulphuretted hydrogen, and exhausting the sulphide of lead with boiling water. It crystallises in confused needles, but more frequently forms a yellow friable mass. It is sparingly soluble in cold, moderately soluble in boiling water. The solutions are yellow and very bitter, and are not altered either by acids or by alkalis. (Probst, *loc. cit.*)

CHEMICAL AFFINITY. *Chemical Attraction, Chemical Force, Elective Attraction, Elective Affinity; Chemische Kraft, Verwandtschaft, Wahlverwandtschaft, Wahlanziehung; Affinitas, Attractio Electiva; Affinité.*—Affinity is that power by virtue of which bodies of dissimilar nature unite together to form compounds of definite constitution, which cannot be destroyed by mechanical agencies, and are, for the most part, dissimilar in properties to the elements from which they are produced. Whether this force is of peculiar nature, distinct from all others, or only a modification of the power which, under various circumstances, shows itself as light, heat, electricity, magnetism, mechanical force, &c., is a question still undecided. That it is intimately related to heat and electricity, is manifest from the whole range of chemical phenomena; indeed no chemical change can take place without a corresponding alteration in the temperature and electrical state of the bodies concerned. The conclusion to which the progress of discovery appears to tend, is that chemical action, heat, electricity, and all other manifestations of force result from certain movements in the ultimate particles of bodies, and are accordingly convertible into the other. This idea will be further developed in the articles HEAT, LIGHT, and ELECTRICITY; for the present, while we are treating of phenomena purely chemical, it will be convenient to speak of affinity as if it were a distinct force.

The terms affinity and chemical combination are not used by all writers in exactly the same sense. L. Gmelin defines affinity as "the power by virtue of which bodies of dissimilar nature combine together into a whole, which appears perfectly uniform to the senses, even when assisted by the most powerful instruments" (*Handbook*, i. 33). Accordingly he applies it to mixtures of liquids, as of alcohol and water, alcohol and volatile oils, &c., and to solutions of solids in liquids, as of salts in water, resins in alcohol, &c., as well as to combinations in definite proportion. Most chemists, however, make a distinction between mixtures and solutions on the one hand, and compounds formed in definite proportions on the other, restricting the term "chemical affinity" to the force, whatever it may be, that is concerned in the formation of the latter. In favour of Gmelin's view, it may be alleged that mixtures of liquids and solutions resemble chemical compounds, commonly so called, in these respects, that they are perfectly uniform in colour, density, refractive power, and other physical characters, and that the force which holds the heterogenous particles together in them is sufficient to resist any tendency to separate arising from difference of density (*e. g.* a mixture of water and alcohol, never separates into two layers, like oil and water), and can only be overcome by the same means as are applied to the destruction of the more intimate kind of combinations, viz. heat, or the superior affinity of another substance, as when resin is precipitated from its solution in alcohol by addition of water, or carbonate of potassium from its aqueous solution by alcohol.

There are, however, several well marked characters by which chemical combination of the more intimate kind, such as that of oxygen and hydrogen in water, hydrogen and nitrogen in ammonia, sulphur and mercury in cinnabar, &c., is distinguished from mere mixture or solution. These distinctions relate to the proportions in which the constituents of the compound are united, to the character of the compound, and to the circumstances attending its formation and decomposition.

1. As regards *proportion*. Mixture and solution follow a law of continuity. Miscible liquids, such as alcohol and water, may be mixed in any proportions whatever, and a solid dissolves in a liquid in all proportions, up to a certain limit, the point of saturation: but chemical combination, properly so called, takes place in certain definite proportions and no others. Thus hydrogen and chlorine unite only in the ratio of 1 pt. by weight of hydrogen to 35·5 pts. of chlorine; oxygen and carbon, only in the ratio of 6 pts. carbon to 8 and 16 pts. oxygen; nitrogen and oxygen, as 14 pts. nitrogen to 8, 16, 24, 32 and 40 pts. oxygen; lead and oxygen as 103·5 lead to 8, $10\frac{2}{3}$, and 16 pts. oxygen, mercury and sulphur as 100 mercury to 8 and 16 pts. sulphur, &c. &c. In all cases, indeed, the number of compounds formed by any two elements is definite, and combination never takes place in any intermediate proportions.

The law which regulates the proportions of the several compounds of the same two bodies is called the "Law of Multiples," and may be thus expressed: The several proportions in which two bodies, A and B, unite, may be represented by the formulæ $A + B$, $A + 2B$, $A + 3B$, . . . $A + nB$, or $2A + 3B$, $2A + 5B$, . . . $3A + 4B$, . . . or in general $mA + nB$; where m and n are integer numbers in most cases not exceeding 7, at least in inorganic compounds.* We have seen in the article ATOMIC WEIGHTS (p. 452), that it was the observation of these proportions which led Dalton to the idea of the atomic theory. In short, if the ultimate atoms of the several elements be supposed to possess certain invariable relative weights, and to unite and form chemical compounds by simple juxtaposition, in the proportion of 1 : 1, 1 : 2, 2 : 3, &c., the law just enunciated follows as a matter of course. It is possible that the distinction between true chemical combination and mixture may be found in this: that combination takes place between ultimate atoms; mixture between the physical molecules of bodies, which are complex aggregates of atoms.

2. As to the *character of the product*.—The properties of a mixed liquid, as the colour, taste, specific gravity, refracting power, &c., are always intermediate between those of its components. In solutions also, the dissolved body imparts to the solvent its taste and colour, in proportion to the quantity dissolved, the density of the solution also increasing regularly and continuously with the amount of solid matter taken up; but definite chemical compounds generally differ altogether in physical properties from their com-

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* The combining proportions of the elements of organic compounds are regulated by much more complex laws. In the series of fatty acids, for example, we find the same quantity of oxygen (8 pts.) associated with 3, 2×3, 3×3, 4×3, 5×3, ... 30×3 parts of carbon; and if, in addition to this, we consider the various proportions of C, H, N, and O, existing in the numerous series of organic bodies, it may fairly be concluded that the constitution of these bodies would never have suggested the law of multiples, as above stated. Indeed, it is only by introducing the hypothesis of compound radicles, that the composition of organic bodies can be assimilated to that of inorganic compounds. (See ORGANIC COMPOUNDS and RADICLES.)

ponents. Thus, with regard to *colour:* yellow sulphur and grey mercury produce red cinnabar; purple iodine and grey potassium yield colourless iodide of potassium; purple iodine and grey lead form bright yellow iodide of lead; the colours of metallic oxides bear no relation whatever to those of the metals themselves, and the compounds of metals with chlorine, iodine, and other salt-radicles, are for the most part transparent, though the metals themselves are opaque. Again, we find organic compounds exhibiting an endless variety of colours, formed by the union of elements which in the free state have no colour at all. The *density* of a compound is very rarely an exact mean between that of its constituents, being generally higher and in a few cases lower; and the *taste, smell, refracting power, fusibility, volatility, conducting power for heat and electricity,* and other physical properties, are not for the most part such as would result from mere mixture of their components. It must not of course be understood that the physical properties of compounds are not related to those of their components by any regular laws. Definite relations doubtless exist, and will one day be discovered: indeed, the regular gradations of boiling point, atomic volume, &c., exhibited by the terms of homologous series of organic compounds, afford striking examples of them; still it is generally true that the properties of a definite compound are not intermediate between those of its components, as in a mixture or solution.

3. As to the *phenomena* which accompany the formation and decomposition of chemical compounds, especially as regards *temperature.* Chemical combination in definite proportions, is always attended with evolution of heat, sometimes amounting to vivid combustion, and decomposition is accompanied by absorption of heat and consequent reduction of temperature; whereas the mere mixing of liquids takes place without change of temperature, and the solution of a solid in a liquid, though partaking of the nature of combination, is attended with reduction of temperature, due to the passage of the body from the solid to the liquid state. So much is this the case, that a rise of temperature attending the contact of a solid and a liquid, may always be regarded as an indication of the formation of a definite compound; thus there are many anhydrous salts, such as chloride of calcium and sulphate of copper, which become strongly heated by contact with water, being at the same time converted into hydrates; but these hydrates, in subsequently dissolving in the water, produce a considerable degree of cold. (See HEAT.)

The formation and resolution of chemical compounds are also attended with changes in the *electrical state* of their elements. Whether the direct combination of two elements produces any electrical disturbance, is not perhaps clearly made out, on account of peculiar difficulties in the investigation of the phenomena (see ELECTRICITY); but the solution of a metal in an acid, which consists in the decomposition of one compound and the formation of another, calls into action a large amount of electric force, which by certain arrangements, hereafter to be considered, may be made to take the form of an electric current. Conversely, an electric current, no matter how developed, whether by chemical action, or by friction, or by magnetic induction, is capable of overcoming the most powerful chemical combinations, and causing the elements to travel through the circuit in opposite directions, and finally separate at the poles of the circuit. No such effect is, however, produced on mixtures or solutions. The passage of an electric current through the solution of a salt, resolves that salt into its elements, but never causes it to separate from the water as a whole.

For these reasons, we shall restrict the term CHEMICAL COMBINATION, to the formation of compounds in definite proportion, and AFFINITY, to the force which is concerned in their production, and proceed to consider more particularly the circumstances and results of chemical combination and decomposition.

Every elementary body is capable of uniting with others, and for the most part with every other. It is true that some of the compounds, as those of carbon with certain metals, of boron with silicon, selenium, and phosphorus, and of iodine with carbon, have either not been formed or are but imperfectly known; but there can be little doubt of the possibility of their formation. The compounds of fluorine with some of the other non-metallic elements are least known, on account of the difficulty of manipulating with fluorine in the free state.

Compounds resulting from the union of two simple substances, are called *binary compounds of the first order;* such are the metallic chlorides, oxides, and sulphides, the chlorides of hydrogen, sulphur, phosphorus, &c. Now, these compounds are capable of uniting with each other in various ways like elementary bodies, and hence result compounds containing three or four elements, which may be regarded as *binary compounds of the second order;* such are double chlorides, $KCl.PtCl^2$; oxygen-salts, as $Ba^2O.SO^3$; sulphur-salts $K^2S.As^2S^3$; hydrated chlorides $CaCl.3H^2O$, &c., and again these compounds of the second order may be conceived as uniting together to form *compounds of the third order*, such as double salts, *e. g.* common alum, which contains sulphate of potassium and sulphate of aluminium, $K^2O.SO^3 + Al^4O^3.3SO^3$. Further than this, the power of combination does not appear to extend.

This view of the successive building up of chemical compounds in binary groups, called the *Dualistic Theory* is, however, not the only one that can be taken, or indeed that which accords best with the present state of knowledge. It is for many reasons better to regard all compounds, whether containing two, three, or more elements, as constituted according to certain typical forms; for example, chlorides, iodides, bromides, and cyanides, as formed on the type of hydrochloric acid HCl; acids, bases, and salts containing oxygen or sulphur, seleniumn or tellurium, as formed on the type of water HH.O, &c. This is called the *Unitary Theory*. (See CLASSIFICATION, RADICLES, SUBSTITUTION, TYPES, and the various articles in which particular compounds are described.) It is true, indeed, that compounds containing three or more elements may, in many instances, be formed by the direct union of binary compounds of the first order; thus double chlorides and iodides are formed by fusing together the component simple chlorides, or by mixing their aqueous solutions and leaving them to crystallise; sulphur-salts, such as $Na^2S.As^2S^3$, by fusing together the simple sulphides; oxygen-salts also, in some instances, by heating together the so-called anhydrous acid and the base; thus boric anhydride and magnesia fused together in the proper proportion form borate of magnesium, $3Mg^2O.B^2O^3$ or Mg^3BO^3; and anhydrous baryta heated in vapour of sulphuric anhydride, burns and forms sulphate of barium, $Ba^2O.SO^3$ or Ba^2SO^4. But it by no means follows that the arrangement of the atoms in the resulting compound must be the same as in the simpler compounds from which it is formed; thus, while the mode of formation of sulphate of barium just mentioned would lead to the supposition that it is $Ba^2O.SO^3$, other modes of formation, and most of its reactions, indicate rather that its constitution is represented by the formula $Ba^2.SO^4$ or $SO^2.Ba^2.O^2$.

These observations apply chiefly to inorganic compounds. Organic bodies, with the exception of cyanogen and the hydrocarbons, all contain at least three elements, and the dualistic view of the building up of compounds by pairs cannot be applied to them at all, excepting on the supposition that they contain certain compound radicles, such as *ethyl*, C^2H^5, *benzoyl*, C^7H^5O, &c., which play the same part as metals in inorganic compounds, uniting like simple radicles, with oxygen, chlorine, bromine, &c. With the help of these radicles, some of which have been obtained in the free state, the constitution of the best known organic compounds, such as the alcohols, ethers, aldehydes, acetones, and their derivatives, may be assimilated to that of inorganic compounds, and represented either on the unitary or the dualistic view.

Formation and Decomposition of Chemical Compounds.

As chemical combination involves a total change in the arrangement of the atoms of the combining bodies, it is clear that cohesion, which tends to hold them in certain fixed positions, must be opposed to chemical union, and on the contrary, anything which gives mobility to the particles of the two bodies, and enables them to intermix and approach within small distances of each other, such as pulverisation, and more especially liquefaction, must tend to promote it.

a. Generally speaking, *one at least of the combining bodies must be either in the liquid or in the gaseous state*, and if it be not so at ordinary temperatures, it must be brought into that state by elevation of temperature. Solid bodies either do not combine at all, or their combination is attended with great difficulty, because, from the immobility of their particles, their points of immediate contact are but few, and the exceedingly thin film of compound which may be formed at such points, acts as a partition to prevent further contact and consequently further combination. But by continued rubbing, which renews the points of contact, more complete combination may often be effected: in this manner, finely divided copper may be made to combine with sulphur, the combination being even attended with rise of temperature. If, on the other hand, the compound formed by the two solids is itself fluid, its mobility gives rise to continually renewed contact, and combination goes on. Thus ice under 0° C. unites with chloride of sodium and other salts, and solid amalgam of lead with solid amalgam of bismuth. Crystallised oxalic acid and lime may be made to combine by rubbing them together, because the acid contains more water of crystallisation than the oxalate of calcium produced is able to take up: hence, at the beginning of the action, a little water is set free and dissolves the oxalic acid. In some cases it is sufficient to heat one of the solid bodies till it softens: thus iron surrounded with charcoal and heated to whiteness is slowly penetrated by the charcoal (*Cementation*). When, in consequence of one or both bodies being in the fluid state, combination takes place at the ordinary temperature or a little above it, it is called *solution in the wet way* (*Solutio via humida*): if a higher temperature is required, the process is called *solution in the dry way, fusion* (*Solutio via sicca, Confusio*).

b. Even if one or both of the bodies be in the fluid state, a higher temperature is often necessary to effect the combination.

Melted sulphur will not combine with carbon; the sulphur must be brought in the state of vapour into contact with red-hot charcoal, although the elasticity of the vapour might rather be expected to interfere with the combination. Neutral carbonate of of sodium, in the efflorescent state absorbs carbonic acid very slowly at first, but more and more quickly as it gets heated by the absorption, and ultimately with great violence. Charcoal requires to be heated before it will burn in oxygen gas, that is, before it will combine with the oxygen. At ordinary temperatures, oxygen may be mixed with hydrogen and other inflammable gases without combining with them, but at a red heat, combination takes place immediately. In this case both bodies are fluid, and we might expect that heat, by increasing their elasticity, would rather oppose than favour the combination. The manner in which heat acts in such cases is not precisely understood; but its effect is probably due to the increased rapidity of movement which it gives to the particles. (See HEAT.)

c. In some cases, *light* has the same effect as an elevation of temperature; thus chlorine, under the influence of light, unites directly with hydrogen or carbonic oxide.

d. *Electricity* likewise favours the combination of many substances, especially of gases, acting chiefly, perhaps, by elevation of temperature. In this manner the combination of oxygen with hydrogen, carbonic oxide or carburetted hydrogen, and of chlorine with hydrogen, is easily brought about.

e. In some instances, the *expansion of gaseous bodies* favours their combination with others. Phosphorus undergoes slow combustion in oxygen gas, however low the temperature may be, the action going on more quickly as the gas is more rarefied; a mixture of oxygen and non-inflammable phosphoretted hydrogen gases explodes on expansion.

f. The presence of a *solid body*, particularly a metal, having a great extent of surface, likewise causes, sometimes at ordinary, sometimes at slightly elevated temperatures, the combination of oxygen with inflammable gases and vapours, which would otherwise take place only at a red heat. This property is most strikingly exhibited by platinum; the more finely divided the platinum, the stronger is its action. When the combination of oxygen with inflammable gases take place at its surface, the heat developed raises its temperature and thereby increases its activity, till at length the metal becomes red-hot and then sudden combination occurs. Platinum appears to condense gases, particularly oxygen, on its surface, whereby the heterogenous atoms are made to approach one another and combine. A similar power is possessed by charcoal and other porous bodies (p. 761).

A body in the act of chemical combination often exhibits the power of inducing the same kind of activity in another body and causing it to combine with a third body, thereby forming a compound which, under the existing circumstances, would not have been formed without the presence of the first body (Liebig, Ann. Ch. Pharm. xxx. 262). Nitrogen gas does not by itself combine with oxygen, even when heated; but if a mixture of nitrogen and hydrogen be set on fire, the hydrogen burns, producing water, and a portion of the nitrogen combines at the same time with oxygen, producing nitric acid. Pure copper does not dissolve in dilute sulphuric acid, but when combined with zinc and nickel (in German silver), metals which decompose acidulated water, or when combined with three times its weight of zinc only, it dissolves completely together with the other metals. Platinum when alone does not dissolve in nitric acid, but when alloyed with silver it becomes soluble in that acid.

Chemical compounds may be formed, either by direct union of their elements, or by substitution of one element for another in a compound previously existing.

Oxygen unites directly with most other elements, either at ordinary or at elevated temperatures; so likewise do *sulphur*, *chlorine*, *iodine*, and *bromine*. *Hydrogen* unites directly with oxygen and chlorine at elevated temperatures, with the latter also at ordinary temperatures, under the influence of light; *nitrogen* shows but little tendency to unite directly with any other element; *phosphorus* unites readily with oxygen, chlorine, iodine, and bromine at ordinary temperatures; with sulphur and selenium with aid of a moderate heat. *Carbon*, at high temperatures, unites directly with oxygen, sulphur, and many metals, not with any other element. *Boron* and *silicium* combine directly with oxygen at ordinary temperatures, if they are in a state of minute division, more easily when heated; with other elements they exhibit little or no power of direct combination. *Metals* unite directly with oxygen, sulphur, selenium, chlorine, bromine, and iodine, sometimes at ordinary, sometimes at higher temperatures; in some instances also with phosphorus and with carbon. Alloys of definite constitution are also frequently produced by melting different metals together, though the greater number of such products are merely mixtures.

It has been already mentioned that compound bodies can unite with one another directly, forming new bodies of more complex constitution. These combinations are sometimes very energetic, as that of anhydrous baryta heated in the vapour of sulphuric anhydride, which is a true case of combustion.

Altogether, however, the cases in which compounds are formed by direct union of elements is small compared with that in which new compounds result from the transformation of others previously existing. Such transformations may be effected in various ways.

I. By *heat*, which may either expel one or more of the elements of the original compound in the free state, leaving the rest in a new form of combination, or may cause the whole of the elements to arrange themselves in the form of new compounds.—1. Chlorate of potassium, $KClO^3$, exposed to a full red heat, gives off the whole of its oxygen, and is converted into chloride of potassium, KCl. Similarly with other chlorates, also with bromates and iodates. Many metallic oxides and sulphides, when heated to redness, give off part of their oxygen or sulphur, and are reduced to lower oxides or sulphides.—2. Chlorate of potassium exposed to a degree of heat less than sufficient to expel the whole of the oxygen, is resolved into perchlorate and chloride of potassium: $3KClO^3 = KCl + 2KClO^4 + O$. Nitrate of ammonium, $NH^4.NO^3$, is resolved by heat into water, $2H^2O$, and nitrous oxide, N^2O. To this head likewise belong the numerous transformations of organic compounds, resulting from dry or destructive distillation.

II. By *electricity.*—The action of the electric current on chemical compounds, either in the fused state or in solution, gives rise to an endless variety of new products. In some instances, the elements of a compound are eliminated by electrolysis in the free state, as when water, hydrochloric acid, or certain metallic oxides, chlorides, or iodides are subjected to the action of the current; frequently, however, the elements arrange themselves in new combinations. We shall consider this subject more fully under ELECTRICITY; at present we will merely mention the formation of peroxide of lead at the positive pole, when a solution of nitrate or acetate of lead is electrolysed; the evolution of arsenetted hydrogen in the electrolysis of aqueous arsenious acid; and the decompositions of acetic acid and other fatty acids, into alcohol-radicles, hydrocarbons of the ethylene-series, carbonic anhydride, and hydrogen.

III. *By the action of another substance, simple or compound.*

a. The decomposing substance is an element (or a compound acting as such), and takes the place of one element of the compound, which is thereby eliminated. This is SIMPLE SUBSTITUTION.

Zinc decomposes hydrochloric acid, HCl, forming ZnCl, and expelling hydrogen. Potassium decomposes water, HHO, expelling half the hydrogen, and forming hydrate of potassium, KHO. Chlorine decomposes bromide of silver, forming chloride of silver and eliminating bromine. Metals in numerous instances displace other metals from solutions of their salts, *e. g.* iron decomposes nitrate of copper, forming nitrate of iron and a deposit of copper. Silicic anhydride, SiO^2, decomposes carbonate of soda, $Na^2O.CO^2$, expelling carbonic anhydride, and forming silicate of soda, $Na^2O.SiO^2$, though not exactly in the proportion here indicated. Boric anhydride, B^2O^3, heated with hydrate of barium expels 3 atoms of water, and forms borate of barium: $B^2O^3 + 3(H^2O.Ba^2O) = 3Ba^2O.B^2O^3 + 3H^2O$.

b. The acting body sometimes enters into combination with both elements of the compound, or with the compound as a whole.

Sulphide of carbon burnt in oxygen, produces sulphurous and carbonic anhydrides. Hydrocarbons and organic compounds in general, yield by combustion, carbonic anhydride and water. Chlorine converts metallic sulphides into chloride of sulphur and metallic chlorides. Chlorine passed into water forms hydrochloric and hypochlorous acids; it decomposes metallic oxides in like manner, forming with mercuric oxide, Hg^2O, for example, chloride of mercury, 2HgCl, and hypochlorous anhydride, Cl^2O. Sometimes only one compound is formed: as when a metallic sulphide is heated in the air and converted into a sulphate: *e. g.* $Cu^2S + O^4 = Cu^2SO^4$; or again, when phosphoretted hydrogen, PH^3, is converted by combustion into phosphoric acid, PH^3O^4.

c. The substance by which the compound AB is decomposed, is itself a compound CD, and the transformation consists in an interchange of elements, whereby the two new compounds AD and BC, are produced. This is DOUBLE DECOMPOSITION. It is the most frequent of all kinds of chemical action, and, as we shall presently explain, may be regarded as typical of the rest. Instances of it may be adduced without number, such as the mutual decomposition of neutral salts, *e. g.* chloride of barium and sulphate of copper; nitrate of silver and chloride of sodium, &c. Also the decomposition of metallic oxides by acids, resulting in the formation of chlorides, iodides, sulphides, &c. and oxygen-salts: thus, with hydrochloric acid and oxide of copper:

$$Cu^2O + H^2Cl^2 = Cu^2Cl^2 + H^2O;$$

hydrochloric acid and hydrate of potassium:

$$KHO + HCl = KCl + HHO;$$

sulphydric acid and oxide of lead:

$$H^2S + Pb^2O = H^2O + Pb^2S.$$

Sulphuric acid and protoxide of iron:

$$H^2SO^4 + Fe^2O = Fe^2SO^4 + H^2O;$$

sulphuric acid and sesquioxide of iron:

$$3H^2SO^4 + Fe^4O^3 = Fe^4(SO^4)^3 + 3H^2O.$$

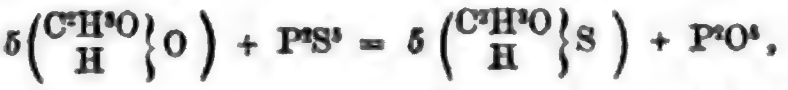
Similarly when compound radicles are concerned, as in organic compounds: *e.g.* the formation of water and chloride of ethyl by the mutual action of alcohol and hydrochloric acid:

$$\left.\begin{matrix}C^2H^5\\H\end{matrix}\right\}O + HCl = C^2H^5Cl + H^2O;$$

of ethylsulphuric acid and water, from alcohol and sulphuric acid:

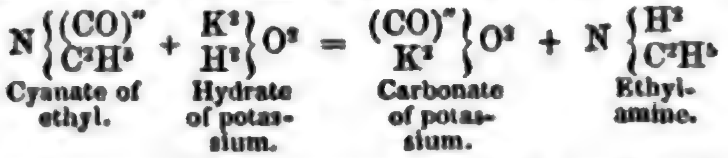
$$\left.\begin{matrix}C^2H^5\\H\end{matrix}\right\}O + \left.\begin{matrix}H\\H\end{matrix}\right\}SO^4 = \left.\begin{matrix}C^2H^5\\H\end{matrix}\right\}SO^4 + \left.\begin{matrix}H\\H\end{matrix}\right\}O;$$

of thiacetic acid and phosphoric anhydride, from acetic acid and pentasulphide of phosphorus:



$$5\left(\left.\begin{matrix}C^2H^3O\\H\end{matrix}\right\}O\right) + P^2S^5 = 5\left(\left.\begin{matrix}C^2H^3O\\H\end{matrix}\right\}S\right) + P^2O^5,$$

of ethylamine by the action of hydrate of potassium on cyanate of ethyl:



$$\underset{\text{Cyanate of ethyl.}}{N\left\{\begin{matrix}(CO)''\\C^2H^5\end{matrix}\right.} + \underset{\text{Hydrate of potassium.}}{\left.\begin{matrix}K^2\\H^2\end{matrix}\right\}O^2} = \underset{\text{Carbonate of potassium.}}{\left.\begin{matrix}(CO)''\\K^2\end{matrix}\right\}O^2} + \underset{\text{Ethylamine.}}{N\left\{\begin{matrix}H^2\\C^2H^5\end{matrix}\right.}$$

In some cases, the decomposition of a compound, AB, is effected by the joint action of two substances C, D, not previously combined; as when an oxide, alumina, for example, is decomposed by the joint action of chlorine and carbon at a red heat, yielding a chloride and carbonic oxide:

$$Al^4O^3 + Cl^6 + C^3 = 2Al^2Cl^3 + 3CO.$$

Sometimes, instead of the two new compounds AD, BC, being produced, only one such compound, AD, is formed, the elements B C being either set free or entering into other combinations. Thus when chloride of ammonium is decomposed by quick lime, the products should be chloride of calcium and oxide of ammonium; but the latter is immediately resolved into ammonia and water:

$$2NH^4Cl + Ca^2O = 2CaCl + (NH^4)^2O\ [= 2NH^3 + H^2O].$$

Aluminium and other sesquiatomic metals do not form carbonates: hence, when a salt of aluminium is precipitated by an alkaline carbonate, the precipitate consists, not of carbonate of aluminium, but of alumina (hydrated), while carbonic anhydride is set free:

$$2Al^2Cl^3 + 3Na^2CO^3 = 6NaCl + Al^4O^3 + 3CO^2.$$

Many peroxides heated with hydrochloric acid, yield water, a protochloride of the metal, and free chlorine, the metal not forming a chloride analogous in composition to the peroxide:

$$MnO + 2HCl = H^2O + MnCl + Cl$$

In many cases, one or both of the new products, AD, BC, enters into combination with an undecomposed portion of one or both of the original compounds, the particular products formed depending upon the proportion in which the original substances are present, and on the circumstances of the experiment. Thus, when sulphide of carbon is decomposed by potash, the immediate products are sulphide of potassium and carbonic anhydride; but these unite with portions of the original substances, forming carbonate and sulphocarbonate of potassium:

$$3CS^2 + 3K^2O = K^2O.CO^2 + 2(K^2S.CS^2).$$

Sulphide of antimony fused with potash, yields at first sulphide of potassium and oxide of antimony; but the final products are oxysulphide of antimony and sulphantimonite of potassium:

$$3Sb^2S^3 + 3K^2O = Sb^2O^3.Sb^2S^3 + 3K^2S.Sb^2S^3;$$

but when 4 at. trisulphide of antimony are fused with 7 at. potash, the products are 2 at. sulphantimonite and 1 at. acid antimonite of potassium:

$$4Sb^2S^3 + 7K^2O = 2(3K^2S.Sb^2S^3) + K^2O.2Sb^2O^3.$$

It has already been stated that double decomposition may be viewed as a type of chemical action in general; in fact, all cases of simple substitution, and even of the direct union of two elements, or the separation of the elements of a binary compound, may be viewed as double decompositions, provided we make certain suppositions respecting the constitution of elements in the free state.

There are many considerations which tend to show that the atoms of an elementary body, or of a compound radicle in the free state, are associated by pairs in a similar manner to the heterogenous atoms of a binary compound; that is to say, a molecule of free hydrogen consists of HH, and a molecule of free ethyl of $C^2H^5.C^2H^5$, just as a molecule of hydrochloric acid consists of HCl, and a molecule of chloride of ethyl of $C^2H^5.Cl$. In the voltaic circuit, the metallic conductor exhibits in many respects the same phenomena as the electrolyte, both parts of the circuit becoming heated, and both producing the same deflection of a magnetic needle placed near them: hence it may be inferred, that the metallic conductor consists of a series of similar particles polarised in pairs, just as the electrolyte consists of a series of heterogeneous particles thus polarised. In a circuit composed of zinc, platinum, and hydrochloric acid, the electrolyte may be regarded as consisting of $\overset{-}{\mathrm{Cl}}\overset{+}{\mathrm{H}}\quad\overset{-}{\mathrm{Cl}}\overset{+}{\mathrm{H}}\quad\overset{-}{\mathrm{Cl}}\overset{+}{\mathrm{H}}$ . . . and the metallic part of the circuit of $\overset{-}{\mathrm{Zn}}\overset{+}{\mathrm{Zn}}\quad\overset{-}{\mathrm{Zn}}\overset{+}{\mathrm{Zn}}\quad\overset{-}{\mathrm{Zn}}\overset{+}{\mathrm{Zn}}$ . . . $\overset{-}{\mathrm{Pt}}\overset{+}{\mathrm{Pt}}\quad\overset{-}{\mathrm{Pt}}\overset{+}{\mathrm{Pt}}$ . . . the entire circuit being thus made up of atoms in opposite polar states. This, as will be more fully explained in the article ELECTRICITY, is the most satisfactory idea that can be given of the phenomena of electro-chemical action.

But there are also considerations purely chemical which tend to the same conclusion. Many instances of chemical action are known, in which two atoms of an elementary body or compound radicle unite together at the moment of chemical change, just like heterogeneous atoms.

Thus, when hydride of copper, Cu^2H, is decomposed by hydrochloric acid, cuprous chloride is formed, and a quantity of hydrogen evolved, equal to twice that which is contained in the hydride itself:

$$Cu^2H + HCl = Cu^2Cl + HH.$$

This action is precisely analogous to that of hydrochloric acid on cuprous oxide:

$$Cu^4O + 2HCl = 2Cu^2Cl + H^2O.$$

In the latter case, the hydrogen separated from the hydrochloric acid unites with oxygen; in the former, with hydrogen. When solutions of sulphurous and sulphydric acids are mixed, the whole of the sulphur is precipitated:

$$SO^2 + 2H^2S = 2H^2O + S.S^2,$$

the action being similar to that of sulphurous acid on selenhydric acid:

$$SO^2 + 2H^2Se = 2H^2O + S.Se^2.$$

In the one case, a sulphide of selenium is formed; in the other, a sulphide of sulphur. The precipitation of iodine, which takes place on mixing hydriodic with iodic acid, affords a similar instance of the combination of homogenous atoms. The reduction of certain metallic oxides by peroxide of hydrogen, is another striking example of this kind of action. When oxide of silver is thrown into this liquid, water is formed; the silver is reduced to the metallic state; and a quantity of oxygen is evolved, equal to twice that which is contained in the oxide of silver. It appears, indeed, as if atoms could not exist in a state of isolation. An atom of an elementary body must unite, either with an atom of another element, or with one of its own kind.

Similar phenomena are exhibited by the alcohol-radicles: thus, when zinc-ethyl and iodide of methyl are heated together, double decomposition takes place, the products being iodide of zinc and methyl-ethyl:

$$C^2H^5.Zn + CH^3.I = ZnI + CH^3.C^2H^5;$$

and when zinc-ethyl is heated with iodide of ethyl, a precisely similar action takes place, but attended with formation of free ethyl:

$$C^2H^5.Zn + C^2H^5.I = ZnI + C^2H^5.C^2H^5.$$

In the first case, the ethyl separated from the iodine unites with methyl separated from the zinc; in the second, it unites with another atom of ethyl. The idea of the duality of the molecules of alcohol-radicles in the free state, is likewise in accordance with their observed boiling-points and vapour-densities. (See ALCOHOL-RADICLES, p. 96.)

Further, elementary bodies frequently act upon others as if their atoms were associated in binary groups. Thus chlorine acting upon potash forms two compounds, chloride and hypochlorite of potassium:

$$KKO + ClCl = ClK + ClKO;$$

just as chloride of cyanogen would form chloride and cyanate of potassium. The quantity of chlorine which acts upon an atom of potash, is not 1 at. = 35·5, but 2 at. = 70. Similarly, when metallic sulphides oxidise in the air, both the metal and the sulphur enter into combination with oxygen. Sulphur acting upon potash forms a sulphide and a hyposulphite. Lastly, when zinc-ethyl is exposed to the action of chlorine, iodine, &c., these elements unite separately with the zinc and with the ethyl, thus:

$$C^2H^5Zn + ClCl = C^2H^5Cl + ZnCl.$$

From these considerations it appears that double decomposition, which is generally understood as an action between four elements or groups of elements, may likewise be supposed to take place in cases where only three elements or groups come into play. In like manner we may regard as double decompositions even those reactions which are commonly viewed as the simple combination or separation of two elements, or as the substitution of one element for another. Thus when potassium burns in chlorine gas, the reaction may be supposed to take place between two atoms of chlorine and two atoms of potassium:

$$KK + ClCl = KCl + KCl.$$

Again, the decomposition of cyanide of mercury by heat may be represented thus:

$$CyHg.CyHg = CyCy + HgHg.$$

The simple replacement of one element by another may also be regarded as a double decomposition, by supposing the formation of an intermediate compound. Thus the action of zinc upon hydrochloric acid may be supposed to consist of two stages:

$$ZnZn + HCl = ZnH + ZnCl,$$

and

$$ZnH + HCl = ZnCl + HH.$$

It is true that the formation of the intermediate compound, the hydride of zinc, cannot be actually demonstrated in this case, because it is decomposed as fast as it is formed; but in other cases, the two stages of the action can be distinctly traced. Thus, it is well known that hydrochloric acid does not dissolve copper; but an alloy of zinc and copper, Cu^2Zn, dissolves in it readily, with evolution of hydrogen. Here it may be supposed that the first products are chloride of zinc and hydride of copper, a known compound:

$$Cu^2Zn + HCl = Cu^2H + ZnCl;$$

and that the hydride is afterwards acted upon by the acid in the manner already explained. Again, when zinc and iodide of ethyl are heated together in a sealed tube, iodide of zinc and zinc-ethyl are obtained, thus:

$$ZnZn + (C^2H^5).I = ZnI + Zn(C^2H^5);$$

and the zinc-ethyl, when heated with excess of iodide of ethyl, yields iodide of zinc and free ethyl (p. 857).

It thus appears that all well understood cases of chemical action may be referred to one type, namely, that of an interchange of elements between two previously existing compounds.

d. The transformation of a compound is brought about by a substance which either remains unaltered, or at all events does not enter into combination with either of the elements of the compound. This obscure mode of action, usually called *Catalysis*, or *Contact-action*, is chiefly observed in the transformations of organic compounds, such as the conversion of sugar into alcohol and carbonic acid, and of alcohol into acetic acid under the influence of yeast; of starch into dextrin and sugar by the action of diastase; the conversion of urea into carbonate of ammonium, by contact with animal mucus, &c. The terms Catalysis and Contact-action explain nothing, but as mere names they are sometimes convenient. Many decompositions formerly spoken of as catalytic, are now regarded as double decompositions, dependent on the polarity of homogeneous atoms (p. 837).

Magnitude or Strength of Chemical Affinity.

That the power which causes bodies to unite is exerted with various degrees of intensity, is evident from the whole range of chemical phenomena. Chlorine certainly unites with hydrogen more readily than with nitrogen, and the elements of hydrochloric acid are held together with far greater force than those of chloride of nitrogen. If zinc displaces copper from its solution in hydrochloric acid, and copper cannot displace zinc from such a solution, we cannot resist the conclusion that the affinity of zinc for chlorine in solution is greater than that of copper. But does this show that the former of these affinities is intrinsically and under all circumstances greater than the latter? or may not the relative solubilities of chloride of zinc and chloride of copper, or the cohesion of the metals themselves, have something to do with the result? Or to state the question generally, does each element possess for every other a distinct and specific affinity or combining power, which is always the same, and liable only to be modified in its results by the circumstances under which the bodies are placed,—or is the affinity between each pair of elements itself a variable quantity dependent on pressure, temperature, solubility, volatility, the presence of other bodies, &c. &c.? The older chemists answered the first part of this question in the affirmative. When they found a body A expelling another B from its union with C, they concluded that C had for A a greater affinity than for B.

On this principle they formed what were called *Tables* or *Columns of Affinity*, of which the following may be taken as specimens, the several substances in each being disposed in the order of their supposed affinity for the body at the head of the column:

Sulphur: O; K and the other alkali-metals; Zn; Fe; Sn; Cu; Cl; H; C; Pb; Bi; Sb; Hg; Ag; Pt; Cu^4S; MoS; Au.

Sulphuric acid: Ba^2O; Sr^2O; K^2O; Na^2O; Li^2O (?); Ca^2O; Mg^2O; Pb^2O; NH^3; Fe^2O; Zn^2O; Ni^2O: Co^2O; Cu^2O; Al^4O^3; Fe^4O^3.

Metals: O; F; Cl; Br; I; Se; P; H.

A very slight acquaintance with chemical phenomena is, however, sufficient to show that these so-called Tables of Affinity are merely tables of the order of decomposition under particular circumstances, and that the relative affinity of one body for two others is liable to change from a great variety of circumstances, sometimes even to be reversed. Thus, iron at a red heat decomposes vapour of water, abstracting the oxygen and setting the hydrogen free, whence it might be inferred that the affinity of oxygen for iron is greater than for hydrogen; but if hydrogen gas be passed over red-hot oxide of iron, water is formed and iron set free, indicating an exactly opposite order of affinities. In like manner, potassium heated in an atmosphere of carbonic anhydride, becomes oxidised and sets carbon free; and on the other hand, charcoal strongly heated with potash, abstracts the oxygen and sets potassium free. Carbonic anhydride precipitates silica from a solution of silicate of sodium, and on the other hand silica heated with carbonate of sodium, forms silicate of sodium, and liberates carbonic anhydride; and similarly in numerous other cases.

We must then look to other circumstances besides intrinsic force of affinity to determine whether a particular reaction will take place or not. The most important of these circumstances are:

1. The *elasticity* or the *cohesion* of one of the resulting compounds, and its consequent tendency to assume the gaseous or solid state, and thus to remove itself from the sphere of action.

The examples just mentioned afford striking illustrations of the influence of volatility in determining chemical decomposition. The tendency of the resulting gas or vapour to diffuse itself through the surrounding atmosphere, doubtless contributes greatly to the result; thus, when aqueous vapour is passed over red-hot iron, the hydrogen set free by the decomposition of the water is carried forward by the current of aqueous vapour, and the iron is left free to act upon a fresh portion. The influence of cohesion is clearly seen in precipitations. It is, indeed, a general law that if the solutions of two salts are mixed, and an insoluble compound can be formed from any of their elements, that compound is sure to be produced and to separate from the liquid. Hence the order of decomposition is frequently reversed by the nature of the solvent. Aqueous acetic acid decomposes carbonate of potassium, eliminating carbonic acid; but if the resulting acetate of potassium be dissolved in alcohol, and carbonic acid gas passed through the solution, carbonate of potassium is precipitated and acetic acid passes into solution as acetic ether. A strong solution of caustic potash decomposes carbonate of calcium, forming carbonate of potassium, and leaving lime undissolved; but a solution of 1 pt. carbonate of potassium in 10 pts. of water, is decomposed by agitation with lime, yielding caustic potash and carbonate of calcium. A weak solution of sulphurous acid dissolves iodine, forming hydriodic and sulphuric acids, $H^2SO^3 + I^2 + H^2O = 2HI + H^2SO^4$; but if the quantity of water in the solution be diminished by evaporation, sulphurous anhydride is evolved and hydriodic acid containing iodine remains behind, $H^2SO^4 + 2HI = I^2 + SO^2 + 2H^2O$.

2. *The relative quantities of the acting substances.*—That the relative degrees of affinity of a body for a number of others to which it is simultaneously presented are greatly modified by their relative masses, was first pointed out by Berthollet. The law laid down by that philosopher respecting the action of masses, is this:—*A body to which two different substances capable of acting on it chemically, are presented in different proportions, divides itself between them in the ratio of the products of their*

respective masses, and the absolute strengths of their affinities for the first body. Thus, if we denote by A and B the masses of the two bodies which are present in excess, by α and β the coefficients of their absolute affinities for the body C; and by a and b the quantities of A and B which actually combine with C, the law just stated will be expressed by the proportion:

$$a : b = \alpha A : \beta B.$$

If this view be correct, any alteration, however small, in the relative quantities of A and B, must produce a corresponding alteration in the relative quantities of the two which unite with C. That this is not the case under all circumstances, is shown by the following experiments of Bunsen and of Debus.

Bunsen's experiments (Ann. Ch. Pharm. lxxxv. 137), which were made in such a manner that all the phenomena of combination concerned in them took place simultaneously, lead to the following remarkable laws:

1. When two or more bodies, BB' . . . are presented in excess to the body A, under circumstances favourable to their combination with it, the body A always selects of the bodies BB' . . . quantities which stand to one another in a simple atomic relation, so that for 1, 2, 3 . . . atoms of the one compound, there are always formed 1, 2, 3 . . . atoms of the other; and if in this manner there is formed an atom of the compound AB', in conjunction with an atom of AB, the mass of the body B may be increased relatively to that of B', up to a certain limit, without producing any alteration in the atomic proportion.

When carbonic oxide and hydrogen are exploded with a quantity of oxygen not sufficient to burn them completely, the oxygen divides itself between the two gases in such a manner that the quantities of carbonic anhydride and water produced stand to one another in a simple atomic proportion. The results of Bunsen's experiments are given in the following table, the numbers in which denote volumes:

Composition of Gaseous Mixture.			Quantities of CO and H consumed by Detonation.		Ratio of CO : H.
72·57 CO	. 18·29 H	. 9·14 O	12·18 CO	. 6·10 H	2 : 1
59·93 „	. 26·71 „	. 13·36 „	13·06 „	. 13·66 „	1 : 1
36·70 „	. 42·17 „	. 21·13 „	10·79 „	. 31·47 „	1 : 3
40·12 „	. 47·15 „	. 12·73 „	4·97 „	. 20·49 „	1 : 4

The results were the same whether the explosion took place in the dark, in diffused daylight, or in sunshine; and were not affected by the pressure to which the gaseous mixture was subjected.

The proportions of hydrogen and carbonic oxide consumed in these several experiments, correspond with the composition of five hydrates of carbonic anhydride, containing, respectively:

$$H^2O.2CO^2;\ H^2O.CO^2;\ 2H^2O.CO^2;\ 3H^2O.CO^2;\ 4H^2O.CO^2;$$

but the results cannot be attributed to the actual formation of these hydrates, inasmuch as hydrates of acids containing several atoms of water are incapable of existing at high temperatures.

2. *When a body, A, exerts a reducing action on a compound, BC, present in excess, so that A and B combine together and C is set free; then, if C can, in its turn, exert a reducing action on the newly-formed compound, AB, the final result of the action is, that the reduced portion of BC is to the unreduced portion in a simple atomic proportion.*

In this case, also, the mass of the one constituent may, without altering the existing atomic relation, be increased to a certain limit, above which, that relation undergoes changes by definite steps, but always in the proportion of simple rational numbers.

When vapour of water is passed over red-hot charcoal, the carbon is oxidised and hydrogen is separated; but the process does not go on so far as the complete formation of carbonic anhydride, but stops at the point at which 1 vol. carbonic anhydride and 2 vol. carbonic oxide are formed to every 4 vol. of hydrogen.

In the imperfect combustion of cyanogen—the gaseous mixture being so far diluted that it will but just explode, in order that the temperature may not rise too high, and the result be consequently vitiated by the partial oxidation of the nitrogen — carbonic anhydride and carbonic oxide are formed, and nitrogen set free, likewise in simple atomic proportion. A mixture of 18·05 vol. cyanogen, 28·87 oxygen, and 53·08 nitrogen, gave, by detonation, 2 vol. carbonic oxide, and 4 vol. carbonic anhydride to 3 vol. nitrogen.

In the combustion of a mixture of carbonic anhydride, hydrogen, and oxygen, in which the carbonic anhydride is exposed at the same time to the reducing action of the hydrogen and the oxidising action of the oxygen, the reduced portion of the carbonic anhydride is likewise found to bear to the unreduced portion a simple atomic relation. In the combustion of a mixture of 8·52 carbonic anhydride, 70·33 hydrogen, and 21·15 oxygen, the resulting carbonic oxide was to the reduced carbonic anhydride in the ratio of 3 : 2. After the combustion of a mixture of 4·41 vol. carbonic oxide, 2·96 carbonic anhydride, 68·37 hydrogen, and 24·26 oxygen, the volume of the carbonic oxide converted into carbonic anhydride by oxidation, was to that of the residual carbonic oxide as 1 : 3.

That these remarkable laws had not been previously observed, is attributed by Bunsen to the fact that they hold good only when the phenomena of combination, which are regulated by them, take place simultaneously: for, even if a body *A* were originally to select for combination from the bodies *B* and *C*, quantities bearing to one another a simple atomic relation, but the combination of *A* and *B* were to take place in a shorter time than that of *A* and *C*, it would follow of necessity, that during the whole of the process, the ratio of *B* to *C*, and therefore, also the atomic relations of the associated compounds, would change, so that the observed proportion would be no longer definite. The same result must follow if the bodies which are combining side by side are not homogeneously mixed in the beginning.

With regard to the bearing of these results on Berthollet's law, it might be objected that, in some of the experiments, as in the combustion of a mixture of carbonic oxide, hydrogen, and oxygen, one of the products, viz. the water, is removed from the sphere of action by condensation, and that the circumstances are therefore similar to the removal of an insoluble product by precipitation. It is scarcely conceivable, however, that a reverse action would take place, even if the gaseous mixture were to remain at the temperature which exists during the combustion. Moreover, in the decomposition of vapour of water by red-hot charcoal, the whole of the products remain in the gaseous state.

Debus (Ann. Ch. Pharm. lxxvx. 103; lxxxvi. 156; lxxxvii. 238), has obtained results similar to those of Bunsen, by precipitating mixtures of lime and baryta-water with aqueous carbonic acid, or mixtures of chloride of barium and chloride of calcium with carbonate of sodium. A small quantity of a very dilute solution of carbonate of sodium added to a liquid containing 5 pts. of chloride of barium to 1 pt. of chloride of calcium, threw down nearly pure carbonate of calcium; but when the proportion of the chloride of barium in the mixture was 5·7 times as great as that of the chloride of calcium, 2·3 pts. of the former were decomposed to 1 pt. of the latter. Hence it appears that, in this reaction also, limits exist at which the ratio of the affinities undergoes a sudden change. In these experiments, however, the products are immediately removed from the sphere of action, and the results are therefore not comparable with those which are obtained when all the substances present remain mixed and free to act upon each other.

The latter condition is most completely fulfilled in the mutual actions of liquid compounds, such as solutions of salts, when all the possible products of their mutual actions are likewise soluble; as, for example, when nitrate of sodium in solution is mixed with sulphate of copper. The question to be solved in such cases is this. Suppose two salts AB, CD, the elements of which can form only soluble products by their mutual interchange, to be mixed together in solution. Will these elements, according to their relative affinities, either remain in their original state of combination, as AB and CD, or pass completely into the new arrangement AD and CB?—or will each of the two acids divide itself between each of the two bases, producing the four compounds AB, AD, BC, BD? and, if so, in what manner will the relative quantities of these four compounds be affected by the original quantities of the two salts? Do the amounts of AD and CB, produced by the reaction, increase progressively with the regular increase of AB, as required by Berthollet's theory? or do sudden transitions occur, like those observed in the experiments of Bunsen and Debus?

The solution of this question is attended with considerable difficulty. For when two salts in solution are mixed, and nothing separates out, it is by no means easy to ascertain what changes may have taken place in the liquid. The ordinary methods of ascertaining the composition of the mixture, such as concentration, or precipitation by reagents, are inadmissible, because any such treatment immediately alters the mutual relation of the substances present. In some cases, however, the mixture of two salts is attended with a decided change of colour, without any separation of either of the constituents, and such alterations of colour may afford indications of the changes which take place in the arrangement of the molecules. This method has been employed by Dr. Gladstone (Phil. Trans. 1855, 179; Chem. Soc. Qu. J. ix. 54), who has carefully examined the changes of colour attending the mixture of a great variety of salts, and applied the results to the determination of the effect of mass in influencing chemical action.

Dr. Gladstone's principal experiments were made with the blood-red sulphocyanate of iron, which is formed on adding sulphocyanic acid or any soluble sulphocyanate to a solution of a ferric salt. On mixing known quantities of different ferric salts with known quantities of different sulphocyanates, it was found that the iron was never completely converted into the red salt; that the amount of it so converted depended on the nature both of the acid combined with the ferric oxide, and of the base combined with the sulphocyanogen; and that it mattered not how the bases and acids had been combined previous to their mixture, so long as the same quantities were brought together in solution. The effect of mass was tried by mixing equivalent proportions of ferric salts and sulphocyanates, and then adding known amounts of one or the other compound. It was found that, in either case, the amount of the red salt was increased, and in a regular progression according to the quantity added. When sulphocyanate of potassium was mixed in various proportions with ferric nitrate, chloride, or sulphate, the rate of variation appeared to be the same, but with hydrosulphocyanic acid it was different. The deepest colour was produced when ferric nitrate was mixed with sulphocyanate of potassium; but even on mixing 1 at. of the former with 3 at. of the latter, only 0·194 at. of the red sulphocyanate of iron was formed; and even when 375 at. of sulphocyanate of potassium had been added, there was still a recognisable amount of ferric nitrate undecomposed. The results of a series of experiments with ferric nitrate and sulphocyanate of potassium are given in the following table:

Ferric Nitrate.	Sulphocyanate of Potassium.	Red Salt produced.	Ferric Nitrate.	Sulphocyanate of Potassium.	Red Salt produced.
1 equiv.	3 atoms.	88	1 atom.	63 atoms.	356
1 ,,	6 ,,	127	1 ,,	99 ,,	419
1 ,,	9·6 ,,	156	1 ,,	135 ,,	487
1 ,,	12·6 ,,	176	1 ,,	189 ,,	508
1 ,,	16·2 ,,	195	1 ,,	243 ,,	539
1 ,,	19·2 ,,	213	1 ,,	297 ,,	560
1 ,,	28·2 ,,	266	1 ,,	375 ,,	587
1 ,,	46·2 ,,	318			

The addition of a colourless salt reduced the colour of a solution of ferric sulphocyanate, the reduction increasing in a regularly progressive ratio, according to the mass of the colourless salt.

Similar results were obtained with other ferric salts, viz. with the black gallate, the red meconate and pyromeconate, the blue solution of Prussian blue in oxalic acid, &c., and likewise with the coloured salts of other metals, *e. g.* the scarlet bromide of gold, the red iodide of platinum, the blue sulphate of copper, when treated with different chlorides, &c.

The amount of fluorescence exhibited by a solution of acid sulphate of quinine was found to be affected by the mixture of a chloride, bromide, or iodide, according to the nature and mass of the salt added; and the addition of sulphuric, phosphoric, nitric, and other acids was found to produce a fluorescence in solutions of hydrochlorate of quinine, or of sulphate which had been rendered non-fluorescent by the addition of hydrochloric acid. Solutions of horse-chestnut bark, and of tincture of thorn-apple, yielded similar results.

The conclusions to be drawn from Gladstone's experiments, are as follows:

When two or more binary compounds are mixed under such circumstances that all the resulting compounds are free to act and react, each acid element enters into combination with each basylous element in certain constant proportions, which are independent of the manner in which the different elements are primarily arranged, and are not merely the resultant of the various strengths of affinity of the several substances for each other, but are dependent also on the mass of each of the substances present in the mixture. All deductions respecting the arrangement of substances in solution, drawn from such empirical rules as that the strongest acid combines with the strongest base, must therefore be looked upon as doubtful. An alteration in the mass of any of the binary compounds present, alters the amount of every one of the other binary compounds, and that in a regularly progressive ratio, sudden transitions occurring only where a substance is present, which is capable of combining with another in more than one proportion. This equilibrium of affinities arranges itself in most cases in an inappreciably short time; but, in certain instances, the elements do not attain their final state of combination for hours.

Totally different phenomena present themselves where precipitation, volatilisation, crystallisation, and perhaps other actions occur, simply because one of the substances is thus removed from the field of action, and the equilibrium, which was at first established, is thus destroyed.

The reciprocal action of salts in solution has also been examined by Malaguti (Ann. Ch. Phys. [3] xxxvii. 198; and by Margueritte (Compt. rend. xxxviii. 305), both of whom conclude that each base divides itself between the several acids. Malaguti concludes from his experiments that, in the mutual action of two salts, if nothing separates from the liquid, the decomposition is most complete when the strongest acid and the strongest base are not originally united in the same salt, and that two experiments of this kind, made in opposite ways, must lead to the same final result; that, for example, when 1 at. of acetate of barium is added to 1 at. of nitrate of lead, the quantities of nitrate of barium and nitrate of lead ultimately present in the liquid are the same as when 1 at. nitrate of barium is mixed with 1 at. acetate of lead.

Margueritte finds that two salts in solution decompose each other, even when one of them is already the least soluble of the four salts that may be produced from the acids and bases present. Thus, a saturated solution of chlorate of potassium to which chloride of sodium is added, becomes capable of dissolving an additional quantity of chlorate of potassium, showing that a portion of the chlorate has been decomposed and a more soluble salt formed.

There are, however, certain well known phenomena, which show that this distribution of acids and bases in solution does not always take place. Boric acid colours litmus wine-red; sulphuric acid turns it bright red. Now if sulphuric acid be gradually added to a warm solution of borate of sodium in water which has been coloured blue with litmus, the liquid at first remains blue, because a combination of soda with excess of boric acid is produced; on the addition of more sulphuric acid, boric acid is set free, and colours the liquid wine-red; and not till all the soda has entered into combination with the sulphuric acid does a further addition of that acid give the liquid a bright red colour; but if sulphuric acid were present at the commencement of the action, either in the free state or combined with sulphate of sodium in the form of an acid salt, the bright red colour would appear at once. From the same cause, a solution of sulphate of potassium or sodium to which boric acid has been added, colours litmus only wine-red; but the addition of $\frac{1}{5000}$ of sulphuric acid immediately produces the bright red tint. Hence boric acid does not take soda from sulphuric acid or set that acid free.—Sulphydric acid and carbonic acid exhibit similar relations towards sulphuric acid.—Tincture of litmus is instantly bleached by chlorine-water, but not till after several days by aqueous solution of iodine: now, a solution of chloride of sodium mixed with iodine should, according to Berthollet, produce a mixture containing chloride of sodium with excess of chlorine, and iodide of sodium with excess of iodine. But the orange-yellow mixture colours litmus green (from the yellow of the solution and the blue of the tincture): and a very small quantity of chlorine-water immediately changes this green colour into the orange-yellow of the solution of iodine: this shows that no chlorine had been set free by the iodine.—Ferric phosphate is soluble in hydrochloric acid, but not in acetic acid. From its solution in hydrochloric acid it is completely precipitated by acetate of potassium. Now if the potash had been divided between the hydrochloric and acetic acids, part of the hydrochloric acid would have remained free, and would have held some of the phosphate of iron in solution. (Gm. i. 153.)

The decomposition of soluble by insoluble salts, affords a striking instance of the tendency of atoms to interchange, and of the influence of mass on chemical action. According to H. Rose (Pogg. Ann. xciv. 481; xcv. 96, 284), sulphate of barium is completely decomposed by boiling with solutions of alkaline carbonates, provided that each atom of sulphate of barium is acted upon by at least 15 at. of the alkaline carbonate. When 1 at. of sulphate of barium is boiled with only 1 at. of carbonate of potassium, only $\frac{1}{5}$ of it is decomposed, and only $\frac{1}{11}$ by boiling with 1 at. of carbonate of sodium, further decomposition being prevented by the presence of the alkaline sulphate already formed. If, however, the liquid be decanted after a while, the residue boiled with a fresh portion of the alkaline carbonate, and these operations repeated several times, complete decomposition is effected. Carbonate of barium is converted into sulphate by the action of an aqueous solution of sulphate of potassium or sodium, even at ordinary temperatures. Solution of carbonate of ammonium does not decompose sulphate of barium either at ordinary or at higher temperatures; carbonate of barium is not decomposed by sulphate of ammonium at ordinary temperatures, but easily on boiling. Sulphate of barium is not decomposed by boiling with caustic potash-solution, provided the carbonic acid of the air be excluded; but by fusion with hydrate of potassium it is decomposed, with formation of carbonate of barium, because the carbonic acid of the air cannot then be completely excluded. Hydrochloric and nitric acids, left in contact at ordinary temperatures with sulphate of barium, either crystallised or precipitated, dissolve only traces of it; at the boiling heat, a somewhat larger quantity is dissolved, and the solution forms a cloud, both with a dilute solution of chloride of barium and with dilute sulphuric acid. Sulphate of strontium is dissolved by hydrochloric acid at ordinary temperatures, sufficiently to form a slight precipitate with dilute sulphuric acid, and with chloride of strontium. Sulphate of calcium treated with hydrochloric acid, either cold or boiling, yields a liquid in which a precipitate is formed, after a while, by dilute sulphuric acid, but not by chloride of calcium.

Sulphate of strontium and sulphate of calcium are completely decomposed by solutions of the neutral and acid carbonates of the alkali-metals at ordinary temperatures, and more quickly on boiling, even if considerable quantities of an alkaline sulphate are added to the solution: the decomposition is also effected by carbonate of ammonia, even at ordinary temperatures. The carbonates of strontium and calcium are not decomposed by solutions of the sulphates of potassium or sodium at any temperature; sulphate of ammonium does not decompose them at ordinary temperatures, but readily with the aid of heat.

Sulphate of lead is completely converted into carbonate by solutions of the neutral and acid carbonates of the alkali-metals, even at ordinary temperatures, the neutral carbonates, but not the acid carbonates, then dissolving small quantities of oxide of lead. Carbonate of lead is not decomposed by solutions of the alkaline sulphates, either at ordinary temperatures or on boiling.

Chromate of barium is decomposed at ordinary temperatures by solutions of the neutral carbonates of the alkali-metals, and much more easily by boiling with excess of an acid carbonate of alkali-metal. When equivalent quantities of the chromate of barium and carbonate of sodium are boiled with water, $\frac{1}{7}$ of the whole is decomposed; when the same quantities of the salts are fused together, and the mass treated with water, only $\frac{1}{87}$ of the barium-salt is decomposed. Carbonate of barium is completely converted into chromate by digestion with the solution of an alkaline monochromate; and the decomposition of chromate of barium by neutral alkaline carbonates, even at the boiling heat, is completely prevented by the presence of a certain quantity of an alkaline monochromate.

Selenate of barium is easily and completely decomposed by solutions of alkaline carbonates, even at ordinary temperatures: this salt is somewhat soluble in water, and more readily in dilute acids.

Oxalate of calcium is decomposed by alkaline carbonates, even at ordinary temperatures; but to effect complete decomposition, the liquid must be frequently decanted and renewed. The decomposition takes place rapidly at the boiling heat; but in all cases it is completely prevented by the presence of a certain quantity of a neutral alkaline oxalate. When the salts are mixed in equivalent proportions, $\frac{3}{17}$ of the oxalate of calcium are decomposed at ordinary temperatures, and $\frac{5}{8}$ on boiling. Carbonate of calcium is partially converted into oxalate by the action of a solution of neutral oxalate of potassium at ordinary temperatures, and more quickly on boiling; but the decomposition is never complete, even when the liquid is frequently decanted and renewed. —Oxalate of lead is completely converted into carbonate at ordinary temperatures by the solution of an alkaline carbonate, a small portion of the carbonate of lead dissolving in the liquid. (Rose.)

The preceding experiments exhibit in a remarkable manner the influence of difference of solubility in determining the order of decomposition. Sulphate of barium is less soluble than the carbonate, and, accordingly, carbonate of barium is more readily decomposed by alkaline sulphates than the sulphate by alkaline carbonates. Precisely the contrary relations are exhibited by the sulphates and carbonates of strontium[*] and calcium, both as regards solubility and order of decomposition. On the other hand, oxalate of calcium is less soluble than the carbonate, and yet its decomposition by alkaline carbonates takes place more easily than the opposite reaction; in this case, the order of decomposition appears rather to be determined, as in Malaguti's experiments (p. 862), by the tendency of the strongest acid to unite with the strongest base.

The effect of a soluble sulphate, &c. in arresting the decomposition of the corresponding insoluble salts by alkaline carbonates, is evidently due to its tendency to produce the reverse action: hence the acceleration produced by decanting and renewing the liquid. Some insoluble salts, however, phosphate of calcium for example, are never completely decomposed, even by this treatment. (See also Malaguti, Ann. Ch. Phys. [3] li. 328.)

Theories of Chemical Action.

Chemical combination was in early times attributed to the general principle of Hippocrates that "like assorts with like:" hence the word *Affinity*, which seems to have been first employed by Barchhusen. Becher assumed, in accordance with this dogma, that when two bodies are capable of combining, they must contain a common

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[*] According to Fresenius, carbonate of strontium dissolves in 11,862 parts, and sulphate of strontium in 6895 parts of water.

principle. Others, among whom was Lemery, supposed that solvents are furnished with a number of sharp points, by means of which they are more or less adapted to insinuate themselves into the pores of solid bodies and combine with them.

Dismissing these crude notions, we have to consider four distinct hypotheses which have been proposed to account for the phenomena of chemical action.

1. *Chemical combinations are produced by universal attraction.*

Newton was the first who referred chemical combination to universal attraction, though he did not regard the attraction between ultimate particles as exactly the same with that which acts between the great bodies of the universe.

Berthollet also regarded chemical combination as a manifestation of the force of universal attraction, exhibiting peculiar characteristics, because it is exerted, not on masses, but on molecules placed at extremely small distances from each other. Being unacquainted with the laws of combination in definite proportions, he supposed that bodies, by virtue of their affinity, are essentially capable of uniting in all proportions, and attributed what he considered the apparent exceptions to the law, entirely to the influence of cohesion and elasticity. That these causes exert considerable influence on chemical combination, is sufficiently evident from the phenomena already discussed; but to suppose that combination in definite proportion is absolutely dependent upon them, would be inconsistent with our present knowledge of the constitution of chemical compounds; indeed, the single fact that chlorine and hydrogen unite in one proportion only, and form hydrochloric acid gas, without any condensation or expansion, is quite sufficient to show the untenability of such a supposition.

2. *Chemical combinations are produced by a peculiar power called Affinity, distinct from all others.* This hypothesis may be reserved for discussion after it has been shown that all the known powers of nature are insufficient to account for the phenomena of chemical action.

3. *The union of heterogenous atoms is the result of Electrical attraction.*

Numerous theories of this kind have been proposed, among others by Davy, Dumas, Becquerel, Ampère, Grotthuss, Schweigger, Fechner, Berzelius and L. Gmelin.

Berzelius supposed that "The atom of every substance has two poles, on which the opposite electricities are accumulated in different proportions, according to the nature of the bodies. The atom of many bodies, oxygen for instance, has a large quantity of negative electricity attached to one of its poles, and but a very small quantity of positive electricity at the other; that of other bodies, potassium for example, has a large quantity of positive electricity at one pole, and a very little negative electricity at the other. Thus the elementary substances are divided into *electro-negative* and *electro-positive.* To each element, however, there belongs a particular proportion between the quantities of the two electricities. Oxygen has, of all the electro-negative elements, the greatest quantity of negative electricity at one of its poles, and the smallest quantity of positive electricity at the other,—then follows sulphur, then nitrogen, &c., and lastly hydrogen, in which the quantities of the two electricities are nearly equal. Of all electro-positive substances, potassium has the largest quantity of positive and the smallest of negative electricity; and this inequality continually diminishes in other bodies, till we come to gold, in which the positive electricity predominates but little over the negative—so that this element occupies the next place to hydrogen. According to this, the elements succeed one another in the electro-chemical series of Berzelius as follows, beginning with the electro-negative.

"*Electro-negative*, O, S, N, F, Cl, Br, I, Se, P, As, Cr, V, Mo, W, B, C, Sb, Te, Ta, Ti, Si, H.

"*Electro-positive*, Au, Os, Ir, Pt, Rh, Pd, Hg, Ag, Cu, U, Bi, Sn, Pb, Cd, Co, Ni, Fe, Zn, Mn, Ce, Th, Zr, Al, Y, G, Mg, Ca, Sr, Ba, L, Na, K.

"In the combination of an electro-negative with an electro-positive body, the predominant negative electricity of the former unites with the predominant positive electricity of the latter. Before, however, combination takes place, the former substance exhibits negative, and the latter positive electricity in the free state; and the tension of the two electricities continually increases as the bodies approach the temperature at which combination takes place. Hence we have an explanation of *electricity by contact.* At the instant of combination, the negative poles of the atoms of the first body turn themselves towards the positive poles of those of the second; and since it is only in the fluid state that the atoms possess the mobility necessary for this arrangement, it follows that solid bodies have, generally speaking, no chemical action on one another The two electricities of these poles now combine and produce heat or fire, whereupon they disappear. In every chemical combination, therefore, a neutralisation of the opposite electricities takes place, by which heat or fire is produced in the same manner as in the discharge of the electrical pile or of lightning, excepting that these last-mentioned phenomena are not accompanied by any chemical combination, at least of ponderable bodies. Every chemical combination is therefore an electrical phenomenon depending on the electrical polarity of the atoms."

The main difficulty of this theory is to account for the force by which combined atoms are held together. The heterogeneous atoms unite in consequence of their adhesion to the opposite electricities; but when these have been neutralised by combination, it might be expected that the atoms would fall asunder and allow themselves to be easily separated by friction and other mechanical forces, which is not the case. This objection to the theory of Berzelius has never been satisfactorily answered.

Gmelin's theory is as follows:—"Ponderable bodies have affinity for one another. The two electricities are substances which likewise possess affinity for each other, and by whose combination in the proportions in which they neutralise each other, heat (fire) is produced. The individual electricities, and likewise heat, have considerable affinity for ponderable substances, and are united to them with greater force and in greater quantity, the more simple these ponderable substances are. Ponderable bodies, according to their nature, have a greater or less excess of positive or negative electricity united with them, in addition to a definite quantity of heat. Thus, oxygen probably contains the greatest quantity of *positive*, and potassium of *negative* electricity. Bodies lying between these two extremes, contain a larger quantity of heat with a smaller excess of one or the other kind of electricity, the proportion of which varies greatly according to their nature.

"The combination of two ponderable bodies is the result of two forces, viz. the affinity of the ponderable bodies for each other, and the affinity of the electricity which is in excess in the one body for the opposite electricity which predominates in the other. By these two forces, the affinity of the electro-negative body for the positive electricity united with it, and that of the electro-positive body for the negative electricity combined with it, are overcome. The result is heat and the ponderable compound. The latter retains the excess of positive or negative electricity, by which it requires either an electro-negative or electro-positive character, and likewise part of the heat—while another portion is set free, and gives rise to the development of heat or fire, by which most chemical combinations are accompanied. When combination takes place between two bodies, both of which contain an excess of the same kind of electricity, *e.g.* oxygen and sulphur, which contain free positive electricity in different quantities,—it is simplest to suppose that the combination is the result merely of the affinity between the two ponderable bodies, that the new compound contains the sum of the excesses of positive electricity, and that the development of heat is a consequence of the inability of the new compound to retain as much heat united with it as was before combined with its constituents." (Gm. i. 154—158.)

4. *Chemical action results from a constant motion among the ultimate particles of bodies, this same movement likewise giving rise to the phenomena of heat, light, and electricity.* This is the theory suggested by Williamson (Chem. Soc. Qu. J. vi. 110). The atoms of all compounds, whether similar or dissimilar, are supposed to be continually changing places, the interchange taking place more quickly as the atoms resemble each other more closely. Thus, in a mass of hydrochloric acid, each atom of hydrogen is supposed, not to remain quietly in juxtaposition with the atom of chlorine with which it happens to be first united, but to be continually changing places with other atoms of hydrogen, or, what comes to the same thing, continually becoming associated with other atoms of chlorine. This interchange is not perceptible to the eye, because one molecule of hydrochloric acid is exactly like another. But suppose the hydrochloric acid to be mixed with a solution of sulphate of copper (the component atoms of which are likewise undergoing a change of place): the basylous elements, hydrogen and copper, then no longer limit their change of place to the circle of atoms with which they were at first combined, but the hydrogen and copper likewise change places with each other, forming chloride of copper and sulphuric acid. Thus it is that, when two salts are mixed in solution, and nothing separates out in consequence of their mutual action, the bases are divided between the acids, and four salts are produced. If, however, the analogous elements of the two compounds are very dissimilar, and, consequently, interchange but slowly, it may happen that the stronger acid and the stronger base remain almost entirely together, leaving the weaker ones combined with each other. This is strikingly seen in a mixture of sulphuric acid (sulphate of hydrogen) and borate of sodium, which soon becomes almost wholly converted into sulphate of sodium and free boracic acid (borate of hydrogen).

Now, suppose that, instead of sulphate of copper, sulphate of silver is added to the hydrochloric acid. At the first moment, the interchange of elements may be supposed to take place as above, and the four compounds, H^2SO^4, Ag^2SO^4, HCl, and AgCl, to be formed; but the last being insoluble, is immediately removed by precipitation; the remaining elements then act upon each other in the same way, and this action goes on till all the chlorine or all the silver is removed in the form of chloride of silver; if the original compounds are mixed in exactly equivalent proportions, the final result is the formation of only two salts, viz. in this case, $H\,SO^4$ and AgCl. A similar result is produced when one of the products of the decomposition is volatile at the existing temperature, as when hydrate or carbonate of sodium is boiled with chloride of ammonium.

If no precipitation or volatilisation takes place, and one of the compounds (hydrochloric acid) is in excess of the other (sulphate of copper), then, as the atoms of copper in their several interchanges must come in contact with chlorine-atoms more frequently than with SO^4-atoms, the final result must be the formation of a larger quantity of chloride of copper and of sulphate of hydrogen than if the bodies had been mixed in equivalent proportions, this effect of course increasing as the relative quantity of hydrochloric acid is greater in the original mixture; and thus we have an explanation of the effect of mass in chemical reaction.

The same theory affords an easy explanation of certain chemical changes otherwise somewhat obscure. Consider, for example, the formation of ether by the action of sulphuric acid upon alcohol, whereby ethyl-sulphuric acid (sulphate of ethyl and hydrogen) is first formed, and afterwards, at a certain temperature, ether and water are eliminated (p. 76). When alcohol, $\left.\begin{matrix}C^2H^5\\H\end{matrix}\right\}O$, and sulphuric acid, $\left.\begin{matrix}H\\H\end{matrix}\right\}SO^4$, are mixed together, the interchange between the atoms of ethyl in the former and of hydrogen in the latter gives rise to the formation of ethyl-sulphuric acid and water:

$$\left.\begin{matrix}C^2H^5\\H\end{matrix}\right\}O + \left.\begin{matrix}H\\H\end{matrix}\right\}SO^4 = \left.\begin{matrix}C^2H^5\\H\end{matrix}\right\}SO^4 = \left.\begin{matrix}H\\H\end{matrix}\right\}O.$$

But the change does not stop here: for the ethyl-sulphuric acid thus produced, meeting with fresh molecules of alcohol, exchanges its ethyl for the hydrogen of the alcohol, producing ether and sulphuric acid:

$$\left.\begin{matrix}C^2H^5\\H\end{matrix}\right\}SO^4 + \left.\begin{matrix}C^2H^5\\H\end{matrix}\right\}O = \left.\begin{matrix}C^2H^5\\C^2H^5\end{matrix}\right\}O + \left.\begin{matrix}H\\H\end{matrix}\right\}SO^4.$$

The sulphuric acid is thus restored to its original state, and is ready to act upon fresh quantities of alcohol; so that if alcohol be allowed to run into the mixture in a constant stream, the temperature being kept within certain limits (between 130° and 140° C.), the process goes on without interruption, ether and water continually distil over, and the same quantity of sulphuric acid suffices for the etherification of an unlimited quantity of alcohol. This is the peculiarity of the process; it has given rise to a variety of explanations, all more or less unsatisfactory, the discussion of which would be foreign to the present purpose; it is sufficient to remark that the hypothesis of atomic interchange affords a ready explanation of the chief peculiarity of the reaction, viz. the formation and decomposition of ethyl-sulphuric acid following each other continuously, without any change of temperature or other determining cause. If it be admitted that the atoms of ethyl and hydrogen in the mixture are continually interchanging in all possible ways, this series of alternate actions follows as a necessary consequence.

The idea of atomic motion is in accordance with physical as well as chemical phenomena. To suppose that rest, rather than motion, is the normal state of the particles of matter, is at variance with all that we know of the effects of light, heat, and electricity. In the theory of heat, the particles of bodies are supposed to be affected with progressive, as well as with rotatory and vibratory movements; and this same hypothesis of progressive movement, which of course implies change of relative position amongst the particles, affords, as already stated, an easy explanation of certain chemical reactions otherwise difficult to understand.

CHENOCHOLIC ACID. $C^{27}H^{44}O^4$. — An acid obtained by boiling taurochenocholic acid, the sulphuretted acid of goose-bile, with baryta-water, and decomposing the resulting barium-salt with hydrochloric acid. It is insoluble in water, but soluble in alcohol and ether, whence it separates as an amorphous mass. The solutions have an acid reaction, and give the characteristic blood-red colour with sugar and sulphuric acid. It is insoluble in cold potash, but when heated with it, forms a salt which, when freed from excess of potash, dissolves readily in water and in alcohol. The *barium*-salt consists of $C^{27}H^{43}BaO^4$. (Heintz and Wislicenus, Pogg. Ann. cviiii. 547.)

CHENOCOPROLITE. An impure iron sinter, containing a little silver and arsenate of cobalt. It is a product of decomposition, not a distinct mineral.

CHENOPODIUM. The herb of *Chenopodium ambrosioïdes* yields by distillation, a pure greenish-yellow volatile oil (about 1½ oz. from 10 lb.) having an aromatic and cooling taste (H. Becker, Zeitschr. Pharm. 1854, p. 8). According to Hirzel (*ibid.*) this oil, dehydrated by chloride of calcium and rectified, yields a colourless distillate boiling at 179° to 181° C.

Chenopodium maritimum.—The ash of this plant, growing on a strip of land reclaimed from the sea, has been analysed by Harms (Ann. Ch. Pharm. xciv. 247) with the following results: *a.* Flowers and young shoots. *b.* Stems.

	K^2O	Na^2O	Ca^2O	Mg^2O	Fe^4O^3	CO^2	SO^3	SiO^2	NaCl	
a.	4·4	2·3	4·2	6·6	4·3	0·9	3·0	2·4	71·9	= 100
b.	3·1	5·0	4·4	2·0	2·5	0·8	3·3	2·0	76·9	= 100

Traces of manganese were also found. The flowers and young shoots are said to yield 31·9 per cent. ash, and the stems 24·3 per cent. This, together with the very large proportion of chloride of sodium in the ash, seems to show that the plants analysed were saturated with salt water. *Aster tripolium* grown on the same soil, likewise yielded a very large amount of ash, containing about 65 per cent. NaCl in the stem and leaves, and 30 per cent. in the flowers.

Chenopodium olidum.—This plant contains an alkaloid having the composition C^3H^9N, either trimethylamine or propylamine, to which its fœtid odour appears to be due. (Dessaignes, Compt. rend. xxxiii. 358.)

Chenopodium Quinoa.—According to Völcker (Chem. Gaz. 1851, p. 129) quinoa seeds dried at 100° C. contain 46·10 per cent. starch, 6·10 sugar and extractive matter, 4·60 gum, 5·74 oil, 8·91 casein with a little soluble albumin, 13·95 insoluble albumin and other albuminoïdal compounds, 9·53 vegetable fibre, 5·05 ash. The ash (after deduction of sand and charcoal) contained 36·76 per cent. potash, 1·31 chloride of sodium, 2·45 lime, 13·61 magnesia, 1·78 ferric oxide, 38·99 phosphoric anhydride, 3·36 sulphuric anhydride, and 2·19 silica.

CHERT. A term often applied to hornstone and to any impure flinty rock, including the jaspers. (See *Ure's Dictionary of Arts, Manufactures and Mines*, i. 655.)

CHESSYLITE or **CHESSY COPPER.** Syn. with AZURITE. (See CARBONATES OF COPPER, p. 784.)

CHESTERLITE. See FELSPAR.

CHESTNUT. *Castanea vesca.*—The fruit of this plant has been examined by Payen (J. Pharm. [3] xvi. 279) and by Albini (Wien. Akad. Ber. xiii. 502). Payen found in 100 pts.:

	Water.	Ash in dry Substance.	Nitrogen.		
			In fresh Substance.	In dry Substance.	After deducting Ash.
Of the cultivated chestnut . .	54·21	4·04	0·53	1·17	1·21
Of the wild chestnut . . .	48·06	3·21	0·50	0·96	0·99

Albini found in the shelled kernels of dried chestnuts from various parts of Italy: 3·0—3·3 per cent. ash, 1·2—2·1 fat, 23·2—38·0 starch, 22·8—23·3 dextrin, 17·5—17·9 sugar, 6·5—8·4 cellulose, 0·9—2·1 vegetable albumin, and 5·2—5·3 so-called protein-compounds.

According to Dessaignes (J. Pharm. [3] xxv. 28), chestnuts contain a little asparagine, but no quercite.

The entire fruit of the tree (undried) yields 0·99 per cent. ash, containing in 100 pts. 39·36 K^2O, 19·18 Na^2O, 7·84 Ca^4O, 7·84 Mg^2O, 5·48 Mn^4O^3 [?], 3·88 SO^3, 2·32 SiO^2, 7·33 P^2O^5, 1·9 phosphates of calcium, magnesia, and iron, 4·82 NaCl. (T. Richardson, Jahresber. f. Chem. i. 1074.)

CHIASTOLITE. *Hollow Spar. Macle.* $Al^4O^3.SiO^2$.—A variety of Andalusite crystallised in right rhombic prisms with angles of 91° 35′ and 88° 27′. On looking into the end of the prism, we perceive in the axis of it a blackish prism, surrounded by the other, which is of a greyish, yellowish, or reddish-white colour. From each angle of the interior prism, a blackish line extends to the corresponding angle of the exterior. In each of these outer angles there is usually a small rhomboïdal space, filled with the same dark substance which composes the central prism. The black matter is the same clay-slate with the rock in which the chiastolite is imbedded. Fracture, foliated, with double cleavage. Translucent. Scratches glass. Rubbed on sealing-wax it imparts negative electricity. Specific gravity 2·94. Hardness 3—7·5. Before the blowpipe it is convertible into a whitish enamel. It has been found in Britany, in the Pyrenees, in the valley of Barège, and in Galicia in Spain, near St. Iago de Compostella. The interior black crystal is properly an elongated four-sided pyramid. U.

CHICA. A red dye, obtained from the leaves of *Bignonia Chica.* (See CARAJURU p. 747.)

CHILDRENITE. A phosphate of aluminium and iron (ferrosum) found with apatite at Tavistock in Devonshire, and at Crinnis in Cornwall. Rammelsberg found in two specimens:

	P^2O^5	Al^4O^3	Fe^2O	Mn^2O	Ca^2O	Mg^2O	H^2O	Total.
I. . .	29·36	18·77	30·75	6·12	0·66	—	17·00	102·66
II. . .	28·92	14·44	30·68	9·07	—	0·14	16·98	100·23

(after deducting 3·82 per cent. of insoluble residue in I. and 4·03 in II.)

From the analysis II., which was made with purer material than I., Rammelsberg deduces the formula: $2(4M^2O.P^2O^5) + 2Al^4O^3.P^2O^5 + 15H\ O$, which may be reduced to that of an orthophosphate with hydrate of aluminium and water, viz.: $(M^8al)P^8O^{12}.5alHO + 5aq$. The crystals belong to the trimetric system: $P . \frac{1}{2}P . 3\breve{P}\infty . \bar{P}\infty . \infty P$ and $0P$. Cleavage parallel to P and $\infty\breve{P}\infty$ (Brooke, Rammelsberg). Specific gravity = 3·247. Hardness = 5 (Rammelsberg). The crystals, which are transparent, have a glassy lustre, and vary in colour from yellowish-brown to blackish, are found on the surface of spathic iron ore intergrown with quartz, iron pyrites, and copper pyrites. (Brooke, Ann. Phil. vii. 316.—Rammelsberg, Pogg. lxxxv. 435; Phil. Mag. [4] iv. 118.)

CHILEITE. Syn. with GÖTHITE.

CHILTONITE. Syn. with PREHNITE.

CHINOLINE. C^9H^7N. *Quinoleine, Leucol* (Runge, Pogg. Ann. xxxi. 68.—Gerhardt, Ann. Ch. Pharm. xlii. 310; xliv. 279.—Hofmann, *ibid.* xlvi. 31; liii. 427; lxxiv. 15.—Bromeis, *ibid.* lii. 130.—Laurent, Ann. Ch. Phys. [3] xix. 367.—C. Greville Williams, Ed. Phil. Trans. xxi. [2]; [3] 377; Jahresber. d. Chem. 1855, p. 548; 1856, p. 532.—v. Babo, J. pr. Chem. lxxii. 73.—Gm. xiii. 243).—Runge, in 1839, obtained from coal-tar an organic base to which he gave the name of *leucol.* Gerhardt, in 1842, obtained a similar product, *quinoleine,* by distilling quinine and other organic bases with potash. Hofmann showed that Gerhardt's quinoleine and Runge's leucol were identical. Laurent first pointed out that Gerhardt's quinoleine was a mixture, a fact afterwards established by Gr. Williams, who separated pure chinoline from it, as well as from the mixture of bases obtained from coal-tar. According to later experiments by Williams, however, the chinoline from coal-tar appears to differ in some respects from that which is obtained from cinchonine, &c. Williams has also succeeded in preparing from chinoline (obtained from cinchonine), a fine blue colouring matter likely to be useful in dyeing.

Formation.—Chinoline is produced in numerous reactions:—1. In the dry distillation of coal, passing over with the tar (Runge).—2. By distilling cinchonine, quinine, or strychnine with hydrate of potassium (Gerhardt).—3. By the electrolysis of nitrate of cinchonine (v. Babo).—4. By distilling thialdine with milk of lime (Wöhler and Liebig, Ann. Ch. Pharm. lxi. v.)—5. By the dry distillation of trigenic acid or trigenate of silver (Liebig and Wöhler, *ibid.* lix. 289).—6. By distilling berberine with milk of lime, or hydrate of lead (Bödeker, Ann. Ch. Pharm. lxix. 43). Bödeker also states that chromate of pelosine heated to 100° C. gives off a mixture of chinoline and phenic acid; but according to Williams (Jahresber. d. Chem. 1848. p. 375), the only volatile products of this decomposition are methylamine. dimethylamine, and a pyrrol-base. Williams is of opinion that the production of chinoline in some of the above reactions has been inferred merely from its odour, when, in reality, not a trace of it has been present.

Preparation.—1. From *Cinchonine.* Pulverised cinchonine is gradually added to hydrate of potassium, which is heated in a retort till it melts; the mixture is then raised to a higher temperature till it becomes brown and emits stifling vapours (Gerhardt); and the distillate, which is a mixture of several bases, is boiled with an acid for several days, whereby pyrrhol is driven off. The dry chinoline which afterwards distils over, beginning to boil at 149° C., but not passing over in large quantities till the boiling point rises to 183°, is separated by repeated fractional distillation (about 200 times) into several portions, the lowest of which boils between 154° and 160°, and the highest, which is the largest in quantity, at 271°. Of these fractions, that which distils below 165° contains lutidine, with a little pyridine and picoline; that between 177° and 182° contains collidine, which is also found in the products up to 199°; and the portion which distils above 199°, especially that between 216° and 243°, consists of chinoline and lepidine, the latter being found chiefly in the portion boiling above 270°. To obtain chinoline (and the other bases) perfectly pure, the individual fractions are converted into platinum-salts, and separated by fractional crystallisation. (Williams.)

2. *From Coal-tar Oil.*—*a.* The mixture of phenylamine and chinoline (leucol), obtained from heavy coal-tar oil (see PHENYLAMINE), is dissolved in absolute alcohol, and neutralised with oxalic acid; and the mother-liquor decanted from the oxalate of phenylamine which has crystallised out, is distilled with potash, the receiver being changed as soon as the distillate no longer produces a blue colour with hypochlorite of calcium, and the chinoline which afterwards passes over is collected apart (Hofmann). Chinoline thus obtained, contains lepidine and other bases (Williams).—*b.* Fifty gallons of the oil of very high boiling point, and heavier than water, are treated with sulphuric acid, and the acid liquid is distilled with lime. The portion of the distillate which sinks in water, contains chinoline, lepidine, &c., together with a number of bases of the phenylamine series. The latter are decomposed with nitrite of potassium and hydrochloric acid (see PHENYLAMINE); the acid liquid is distilled from the heavy oil containing phenic acid; the admixed non-basic oils are expelled by passing steam through the liquid; the residue is filtered through charcoal; and the bases are separated from the aqueous solution by potash, and dried over sticks of solid potash. The mixture thus obtained yields, after more than a hundred fractional distillations, portions boiling between 177° and 274°, and from these the chinoline is separated by fractional crystallisation of the platinum-salts, as above. (Williams.)

Properties.—Chinoline is a transparent, colourless, strongly refracting, mobile oil, which neither thickens or freezes at $-20°$ C. (Hofmann, Bromeis). Specific gravity 1·081 at 10° (Hofmann). It conducts electricity less readily than phenylamine (Hofmann), boils steadily at 238° C. and distils without alteration (Williams): it evaporates even at ordinary temperatures, so that the oil-stain which it produces on paper soon disappears. The vapour-density of chinoline boiling between 238° and 243° C. is 4·519 (Williams). Chinoline has a penetrating odour, like that of phosphorus and of hydrocyanic acid (Runge), of St. Ignatius' bean (Gerhardt), of bitter-almond oil (Hofmann). It does not appear to be poisonous (Gerhardt). The aqueous solution kills leeches, but when introduced into the stomach of a rabbit, produces only transient convulsive symptoms and prostration of strength. It is alkaline to litmus and turmeric (Gerhardt, Bromeis); only to dahlia-paper (Hofmann).

Several formulæ have been proposed for chinoline. According to the analyses of Hofmann and Bromeis (made on chinoline containing lepidine, according to Williams), it is C^9H^8N; Gerhardt at first regarded it as $C^6H^{11}NO$, afterwards (*Traité*, iv. 449) as $C^{10}H^9N$. The formula C^9H^7N, first suggested by Laurent, is confirmed by Williams's analyses of several of the salts; the pure base does not appear to have been analysed. The formula C^9H^7N gives for the vapour-density, calculated to two volumes, the number 4·47 which agrees very nearly with Williams's determination.

Chinoline is very sparingly soluble in cold water, rather more in hot *water* and is extracted from the solution by ether (Hofmann). When shaken up with water at 0° C. it forms a clear oil containing $2C^9H^7N.3H^2O$, which at 15° C. gives up water and becomes turbid. When chinoline saturated with water at 0° C. is heated to 100°, water and a little chinoline escape, and a clear hydrate remains, containing $2C^9H^{17}N.H^2O$, which remains limpid and mobile at $-20°$, but is resolved by distillation into water and anhydrous chinoline. (Bromeis.)

Chinoline mixes in all proportions with *sulphide of carbon*, *alcohol*, *ether*, *wood-spirit*, *aldehyde*, and *acetone;* it also mixes with *oils*, both fixed and volatile. It dissolves *phosphorus*, *sulphur*, and *arsenic*, also common *camphor* and *colophony*, but not copal or caoutchouc. It does not coagulate albumin.

Decompositions.—1. Chinoline when set on fire, burns with a luminous but smoky flame.—2. It becomes resinised by exposure to the air.—3. *Chlorine* instantly changes it into a black resin, with great rise of temperature and evolution of hydrochloric acid (Hofmann), into a yellow oil, which is decomposed by water, leaving a white insoluble substance (Williams).—4. With *bromine*, it forms a similar resin (Hofmann).—5. Aqueous chinoline treated with a mixture of *hydrochloric acid* and *chlorate of potassium* rapidly becomes covered with a layer of orange-red oil, which solidifies to a tough mass on cooling (Hofmann).—6. *Fuming nitric acid* acts violently on chinoline, and converts it into a splendid mass of crystals, but does not form any products of decomposition (Gr. Williams).—7. Chinoline immediately takes fire in contact with dry *chromic acid*, and is resinised by aqueous chromic acid (Hofmann).—8. *Permanganate of potassium* decomposes chinoline into oxalic acid and ammonia Hofmann).—*Potassium* dissolves in chinoline, with evolution of hydrogen, but without colouring. On melting potassium in chinoline vapour, cyanide of potassium is formed. Chinoline vapour passed over burnt tartar, remains for the most part unchanged, but forms a small quantity of cyanide of potassium (Hofmann).—10. Chinoline passed over *red-hot quick lime* (Hofmann), or *soda-lime* (Bromeis), suffers little or no decomposition.—11. Enclosed in a sealed tube with *iodide of methyl*, and heated for ten minutes to 100° C., it is changed into crystals of hydriodate of methyl-chinoline. In like manner, it is converted by *iodide of ethyl* into hydriodate of ethyl-chinoline, and by *iodide of amyl* into hydriodate of amyl-chinoline (Williams).—12. Chinoline becomes warm when mixed with *sulphate of methyl* (sometimes disengaging vapour of methylic ether and methylic alcohol), and forms, if complete combination has been promoted by heat, a liquid soluble in water, which, when excess of sulphate of methyl is present, deposits separate crystals. The liquid is rendered turbid by potash or baryta, and separates oil-drops, which at first become red, then green, finally violet, and when heated pass into a beautiful violet resin, *methylirisine*, with formation of sharp, strongly smelling, condensable vapours. At the same time a brown resin and a sulphomethylate are formed. Chinoline, heated to boiling with *sulphate of ethyl*, forms a colourless liquid, which, when boiled with strong caustic potash, deposits a violet resin, *ethylirisine*, insoluble in ether, and a brown resin soluble in ether, while an ethylsulphate remains dissolved, and a sharp neutral oil, sinking in water, passes over, which, if immediately mixed with dichloride of platinum, yields beautiful needles, but soon decomposes (v. Babo).—13. *Chloride of acetyl* acts violently on chinoline, forming a crystalline very deliquescent mass (Williams).—14. With *cyanate of ethyl*, it solidifies into a crystalline mass consisting of phenyl-chinyl-carbamide, $N^2(CO)''.C^6H^5.C^9H^5.H^2$.

CHINOLINE SALTS.—Chinoline unites with acids, forming salts which crystallise easily (Williams). It precipitates salts of aluminium and ferricum, and renders lead-salts and ferrous salts slightly turbid (Hofmann). According to Gerhardt, it precipitates nitrate of silver, but not ferric nitrate.

Chinoline salts are decomposed by fixed alkalis; also by ammonia at a moderate heat; but at high temperatures, chinoline expels ammonia. Dry chinoline-salts treated with phenylamine, emit the odour of chinoline. (Hofmann.)

Chlorhydrate or *Hydrochlorate of Chinoline.*—Chinoline absorbs hydrochloric acid gas violently, and with evolution of heat, and solidifies on cooling to white crystals, which take up more hydrochloric acid, becoming red and liquid, and on again cooling, solidify to a deliquescent, slightly crystalline mass. Hence chinoline appears to form both a neutral and an acid hydrochlorate (Bromeis). When hydrochloric acid gas is passed over chinoline dissolved in ether, the hydrochlorate separates in heavy viscous drops, which after a while become slightly crystalline (Hofmann). Mixed with solutions of metallic chlorides, it forms double salts, which for the most part crystallise readily.

Chlorantimonite.—Chinoline forms with trichloride of antimony a white precipitate, which dissolves in boiling hydrochloric acid, and crystallises on cooling (Hofmann).

Chloro-aurate. $C^9H^7N.HCl.AuCl^3$.—Delicate canary-yellow needles, permanent in the air, sparingly soluble in water, and containing, when dried at 100° C. 41·85 per cent. of gold; the formula requires 42·0 per cent. (Williams.)

Chlorocadmate. $C^9H^7N.HCl.PtCl^2$.—The concentrated solutions of hydrochlorate of chinoline and chloride of cadmium solidify to a pulp when mixed: the dilute solutions yield white permanent needles, which give off 2 at. water at 100° C., volatilise completely at a higher temperature, and are sparingly soluble in alcohol. (Williams.)

Chloromercurate. $C^9H^7N.2HgCl$.—White precipitate, which is not decomposed by boiling water (Hofmann), and separates on cooling in beautiful pearly plates (Bromeis). It smells of chinoline, and has a very bitter, disagreeably metallic taste. According to Hofmann's analysis, it contains 26·5 per cent. C, 17·6 Cl, and 49·9 Hg, the formula requiring 27·0 C, 17·75 Cl, and 50·0 Hg.

Chloropalladite. $C^9H^7N.HCl.PdCl$.—Chestnut-brown crystals, containing 20·96 per cent. Pd; by calculation 21·18 per cent. (Williams.)

Chloroplatinate. $C^9H^7N.HCl.PtCl^2$.—Yellow crystalline precipitate, which dissolves in 893 pts. of water at 15° C. (Williams). The salt obtained by fractional crystallisation, fourteen times repeated, from a portion of the bases (prepared from cinchonine, p. 869), boiling between 238° and 243°, yielded 32·36 per cent. C, 2·74 H, and 29·29 Pt, the formula requiring 32·06 C, 2·58 H, and 29·19 Cl. (Williams.)

Chlorostannite.—Hydrochlorate of chinoline forms with protochloride of tin, a yellow, heavy oil, which afterwards becomes crystalline, and dissolves with difficulty in alcohol. (Hofmann.)

Chloro-uranate. $C^9H^7N.HCl.(U^2O)Cl$.—Concentrated solutions of ammonio-chloride of uranyl and hydrochlorate of chinoline, solidify when mixed: dilute solutions yield beautiful yellow prisms, containing (at 100° C.) 31·87 per cent. C, 2·77 H, and 20·97 Cl, the formula requiring 32·05 C, 2·37 H, and 21·07 Cl. (Williams.)

Chromate of Chinoline. — Chromic acid forms a yellow crystalline precipitate with chinoline (Gerhardt, Hofmann). Dilute chromic acid added in excess to aqueous chinoline (obtained from cinchonine), throws down a small quantity of resinous matter, which becomes crystalline when rubbed with a glass rod, dissolves in boiling water after filtering and washing, and is deposited in brilliant needles on cooling. It detonates when heated, but not after addition of hydrochloric acid. The crystals gave by analysis, 45·08 per cent. C, 3·49 H, and 22·34 Cr, agreeing very nearly with the formula $2C^9H^7N.H^2O.2Cr^2O^3$ (Williams). Chinoline from coal-tar did not yield a crystallised compound with chromic acid, but only oily drops, even when the impurities which could be destroyed by chromic acid had been removed. (Williams.)

Nitrate of Chinoline.—Solution of chinoline in excess of nitric acid, leaves when evaporated over the water-bath, a pasty mass, which solidifies on cooling, and when crystallised from hot alcohol, forms white needles, permanent in the air, infusible at 100° C., and consisting of $C^9H^7N.HNO^3$ (Williams). Easily soluble in water and alcohol, insoluble in ether. (Hofmann.)

Oxalate of Chinoline, is a confused, radiating, unctuous mass, easily soluble in water, alcohol, and ether (Hofmann). An *acid oxalate*, $C^9H^7N.C^2H^2O^4$, is obtained on mixing a solution of 16·5 pts. oxalic acid in a small quantity of water with 243 pts. of chinoline, as a soft, white, crystalline mass, which when recrystallised from alcohol, forms slender needles having a silky lustre. It decomposes at 100° C., with evolution of chinoline. (Williams.)

When chinoline containing phenylamine is dissolved in alcohol or ether, and mixed with alcoholic oxalic acid, almost all the oxalate of phenylamine is deposited after a few hours, while oxalate of chinoline remains in solution. (Hofmann.)

Picrate of Chinoline resembles picrate of phenylamine. (Hofmann.)

Sulphate of Chinoline. — Crystallisable and deliquescent. (Gerhardt and Hofmann.)

Tannate of Chinoline.—Chinoline forms with infusion of galls, a yellowish-brown precipitate (Hofmann); a white flocculent precipitate, soluble in boiling water and in alcohol. (Gerhardt.)

Substitution-Derivatives of Chinoline.

METHYL-CHINOLINE, $C^{10}H^9N = N.H.CH^3.C^9H^5$. (Gr. Williams, Ed. Phil. Trans. xxi. [3] 577.)—Not known in the free state, at least in definite form. The *hydriodate* is obtained in fine crystals, by heating chinoline and iodide of methyl together to 100° C. in a sealed tube for ten minutes. It is decomposed by oxide of silver, forming iodide of silver, and an unstable, strongly alkaline solution, which when heated with potash emits a suffocating odour, probably arising from methylamine. The *platinum-salt*, $C^{10}H^9N.HCl.PtCl^2$, is obtained as a sparingly soluble salt, by decomposing the solution of the hydriodate with nitrate of silver, precipitating the excess of silver with hydrochloric acid, and adding dichloride of platinum to the filtrate.

ETHYL-CHINOLINE, $C^{11}H^{11}N = N.H.C^2H^5.C^9H^5$. (Gr. Williams, *loc. cit.*)

Chinoline treated with iodide of ethyl, as in the preparation of hydriodate of methylchinoline, yields, after distilling off the excess of iodide of ethyl, crystals of hydriodate of ethylchinoline. On treating these crystals with oxide of silver and water (if this is done in the water-bath, a volatile product escapes which attacks the eyes), and filtering off the iodide of silver, a colourless, strongly alkaline solution of ethylchinoline is obtained, which decomposes on evaporation in the water-bath, assuming a carmine colour, and on the edges emerald-green, afterwards changing to a beautiful blue. It expels ammonia from sal-ammoniac. It precipitates chloride of mercury and the salts of lead, iron, and copper.

Hydriodate of Ethylchinoline, $C^{11}H^{11}N.HI$, forms cubes when recrystallised from alcohol. It is more soluble in water than in alcohol. It gives by analysis, 46·5 per cent. C, 4·4 H, and 44·1 I, the formula requiring 46·3 C, 4·9 H, and 44·6 I.

At 100° C., it becomes transiently blood-red. It is decomposed by sulphate of silver, forming iodide of silver, and a liquid which is colourless at first, but on evaporation over the water-bath, assumes a carmine colour, dark blue at the edges, and when dry leaves a blackish-red mass having a coppery lustre. The mass forms with water a dark carmine solution, which is coloured scarlet by hydrochloric and nitric acids, and rose-red by ammonia: with potash, it forms a violet precipitate which is but sparingly soluble in water, but dissolves in alcohol, forming a carmine-red solution. Dichloride of platinum produces in the hydrochloric acid solution of the precipitate, a bulky, insoluble double salt, of a higher atomic weight than the platinum-salt of hydrochlorate of ethylchinoline.

Platinum-salt of Ethylchinoline. $C^{11}H^{11}N.HCl.PtCl$.—Golden-yellow, sparingly soluble precipitate.

Respecting v. Babo's compounds, *methyl-* and *ethyl-irisine*, which appear to be isomeric with methyl- and ethyl-chinoline, see p. 870; also the names of the substances themselves.

AMYL-CHINOLINE, $C^{14}H^{17}N = N.H.C^5H^{11}.C^9H^5$ (Gr. Williams, *loc. cit.*)—A mixture of chinoline and iodide of amyl heated in a sealed tube for several hours to 100° C., deposits beautiful crystals of the hydriodate, $C^{14}H^{17}N.HI$. The *platinum-salt*, $C^{14}H^{17}N.HCl.PtCl^2$, is sparingly soluble in water, insoluble in ether-alcohol.

Hydriodate of amyl-chinoline heated with alkalis, yields a fine blue colour, which may be used as a dye. To prepare it, 1 pt. by weight of crude chinoline is to be boiled for ten minutes with 1½ pts. of iodide of amyl. The mixture, from being straw-coloured becomes deep reddish-brown, and solidifies on cooling to a mass of crystals. This product of the reaction is to be boiled for about ten minutes with 6 pts. of water, and, when dissolved, filtered through paper. The filtered liquid is to be gently boiled in an enamelled iron pan over a small fire, and excess of ammonia gradually added. The ebullition may be prolonged with advantage for one hour, the evaporation of the liquid being compensated for by the gradual addition of weak solution of ammonia, prepared by the admixture of equal volumes of ammonia of the density of 0·880 and distilled water. The hour having elapsed, the whole is allowed to cool, when the colour will almost entirely have precipitated, leaving the supernatant liquid nearly colourless. On pouring the fluid away (preferably through a filter, in order to retain floating particles of colour) the dish will be found to contain resinous looking masses which dissolve readily in alcohol, yielding a rich purplish-blue solution, which may be filtered and kept for use.

The colour prepared as above is of a purplish tint, but if a purer blue be required the following modification is to be resorted to. The filtered aqueous solution of hydriodate of amyl-chinoline, is, as before, to be brought to the boiling temperature; but instead of adding ammonia, a solution of caustic potash containing about one-fifth of its weight of solid potash is to be substituted. The addition is to be continued at intervals until three-fourths as much potash has been added as is equivalent to the iodine in the iodide of amyl used. The fluid may, after a quarter of an hour's ebullition, be filtered to separate the resinous colour. The product is a gorgeous blue with scarcely any shade of red. On adding the other fourth of potash to the filtrate while gently boiling, a black mass will be precipitated containing all the red, which otherwise would have been mixed with the blue. This mass dissolves readily in alcohol, yielding a rich purple solution containing, however, an excess of red. The alcoholic solution, on filtration, leaves on the filter a dark mass soluble in benzene, and as sometimes prepared, affording a brilliant emerald-green solution of great beauty. It is not always easy to obtain this green colour.

It is only the chinoline prepared from cinchonine that yields these colouring matters: a fact which points to an essential difference between this product and the isomeric base found among the products of the distillation of coal. Cinchonine distilled with excess of potash, yields about 65 per cent. of crude chinoline; and all the distillate which, on rectification (p. 869), distils above 199° or 209° C. (390° or 408° F.), up to the highest range of the mercurial thermometer, is suitable for the preparation of the colour. One pt. of this distillate and 1½ pts. iodide of amyl, yield 23 pts. of blue dye containing 4 per cent. of solid colouring matter. (Gr. Williams, *Chemical News*, 1861, p. 219.)

Chinoline-violet and chinoline-blue are resinous substances, which present a coppery appearance by reflected light, but when in very thin layers, appear of a violet or blue colour by transmitted light. They are bases and dissolve in acids, forming pale red solutions, which ammonia restores to their original colours. They are slightly soluble in hot water. Tannin precipitates them from their aqueous solutions, apparently forming an insoluble compound. Reducing agents do not affect their shade of colour. (W. H. Perkin, Chem. Soc. Qu. J. xiv. 246.)

Two volumes of chinoline-blue mixed with 1 vol. of Magenta pink (fuschine), of the ordinary strength found in commerce, form a fine purple inclining to blue (**Williams**). When chlorine is passed through an alcoholic solution of chinoline-blue, a green liquid is produced, which is perhaps the green spoken of by Williams. (Perkin.)

CHINONE. Syn. with QUINONE.

CHIOLITE. A fluoride of aluminium and sodium, $Na^3Al^4F^9$, occurring at Miask in the Ural, in snow-white, translucent, octahedral crystals, of the dimetric system, in which the principal is to the secondary axes as 1·077 : 1; also massive, granular resembling cryolite, with crystalline structure. Specific gravity 2·72 (Hermann); 2·842—2·898 (Rammelsberg). Hardness = 4. Analysis by Hermann (J. pr. Chem. **xxxvii**. 188), gave 23·78 per cent. Na, 18·69 Al, the formula requiring 23·4 and 18·6. Fuses easily before the blowpipe, and gives the reaction of fluorine. (Dana, ii. 98.)

CHITIN (from χιτων, a tunic). (Odier, Mém. Soc. d'Hist. Nat. de Paris, i. 29.—Lassaigne, J. Chim. méd. ix. 379; Compt. rend. xvi. 1087.—Payen, Compt. rend. xvii. 227.—C. Schmidt, *Zur vergleichenden Physiologie der wirbellosen Thiere.* 1845, p. 32; and Ann. Ch. Pharm. liv. 298.—Lehmann, Jahresber. d. ges. Med. 1844, p. 7.—Frémy, Ann. Ch. Phys. [3] xliii. 94; Schlossberger, Ann. Ch. Pharm. xcviii. 99.—Städeler, *ibid.* cxi. 21.—Gerh. *Traité*, iv. 535.—Pelouze et Frémy, *Traité*, vi. 93.)—The name given by Odier to the organic substance which forms the elytræ and integuments of insects and the carapaces of crustacea. It may be obtained by exhausting the wing-cases of cockchafers successively with water, alcohol, ether, acetic acid, and boiling alkalis. The final residue retains completely the form of the wing-cases. Frémy prepares chitin by treating the tegumentary skeleton of a crustaceous animal with cold dilute hydrochloric acid, to remove calcareous salts; washing with distilled water; boiling for several hours with solution of potash, which removes adhering albuminous substances, and has no action upon chitin; again washing with distilled water; and purifying the residue with alcohol and ether.

Chitin thus prepared is solid, transparent, of horny aspect, insoluble in water, alcohol, and ether. It is coloured brown by solution of iodine. Alkalis have no action upon it. By boiling with dilute acids, it is resolved into glucose and a nitrogenous compound. (Städeler.)

When chitin (from the carapace of the crab) is boiled for several hours with dilute sulphuric acid, only the softer membranes are attacked, while the more solid integuments become loose and soft, and form, after pressing and washing with water, a mass having almost the consistence of starch. The acid liquid supersaturated with lime, and then neutralised with sulphuric acid, yields neither tyrosine nor leucine, but contains ammonia, together with amorphous sugar, inasmuch as it precipitates cuprous oxide abundantly from an alkaline solution of cupric oxide (Städeler). Berthelot (Ann. Ch. Phys. [3] lvi. 149) likewise obtained sugar from chitin (prepared from the integuments of lobsters, crabs, and cantharides,) by macerating it in strong sulphuric acid till it was dissolved, dropping the solution into one hundred times its volume of boiling water, boiling for an hour, saturating with chalk, &c.

The above-mentioned pasty residue is coloured brown-red by iodine, like unaltered chitin, and by prolonged boiling with sulphuric acid, yields an additional quantity of sugar, while the undissolved portion always contains nitrogen. The same substance, after removal of the acid, forms with water a turbid emulsion, which takes a long time to clarify, and dries up by spontaneous evaporation to a soft skin-like membrane, which exhibits, with iodine-water, the same reactions as the original chitin. (Städeler.)

The composition of chitin is determined by the following analyses:—

	Schmidt. Mean of 11 analyses.	Lehmann.	Schlossberger.	Städeler.	*Calculation* $C^9H^{15}NO^6$.
Carbon . . .	46·64	46·73	46·64	46·32	46·35
Hydrogen . .	6·60	6·59	6·60	6·65	6·44
Nitrogen . .	6·56	6·49	6·56	6·14	6·01
Oxygen . .	40·20	40·19	40·20	40·89	41·20
	100·00	100·00	100·00	100·00	100·00

Frémy found in chitin 43·35 carbon, 6·65 hydrogen and no *nitrogen*, whence he regards chitin as isomeric with cellulose (44·4 C, 6·2 H, and 49·4 O). Gerhardt regarded Frémy's results as more correct than those of the German chemists, because chitin yields by dry distillation only acetic acid and empyreumatic oil, without any ammonia, and the products of its putrefaction under water are different from those of most nitrogenous substances. But the analyses above given exhibit a closeness of agreement which could scarcely be expected if the substances operated upon had been impure. (See CELLULOSE, p. 818.)

Städeler regards chitin as a glucoside, $C^9H^{15}NO^6$, which is resolved by boiling with acids into glucose and lactamide (or alanine or sarcosine):

$$C^9H^{15}NO^6 + 2H^2O = C^6H^{12}O^6 + C^3H^7NO^2.$$

If this decomposition really takes place, lactic acid should likewise be obtained as a product of the transformation of the lactamide or alanine; but the presence of lactic acid among the products has not yet been demonstrated. Städeler also suggests that chitin (at least in crustacea) may be formed by the union of lactate of ammonium with gum, and elimination of water:

$$[\underset{\substack{\text{Acid lactate of}\\\text{ammonium}}}{C^3H^4O^3.H.NH^4} + \underset{\text{Gum.}}{C^6H^{10}O^5} = \underset{\text{Chitin.}}{C^9H^{15}NO^6} + 2H^2O],$$

inasmuch as he has found gum in the juices of crabs and other crustacea, and the presence of lactic acid in the gastric juice of the lower animals is by no means improbable.

CHIVIATITE. A sulphide of lead and bismuth, also containing copper, from Chiviate in Peru, where it occurs, with pyrites and heavy spar, in foliated masses, cleavable in three directions in one zone, one making an angle with the second of 153°, and with the third of 133°. Specific gravity 6·920; colour lead-grey; lustre metallic. According to Rammelsberg's analysis (Pogg. Ann. lxxxviii. 320) it contains 18·00 S, 60·95 Bi, 16·73 Pb, 2·42 Co, 1·02 Fe, with trace of silver, and 0·59 insoluble matter (= 99·71), whence the formula $2(Pb^2;Cu^2)S.Bi^2S^3$. (Dana, ii. 77.)

CHLADNITE. See METEORITES.

CHLOANTHITE. Native arsenide of nickel containing cobalt, also called white nickel. (See NICKEL).

CHLOCARBETHAMIDE. Syn. with TRICHLORACETAMIDE (p. 6).

CHLORACETAMIC ACID. Syn. with TETRACHLORACETAMIDE (p. 6).

CHLORACETAMIDE. See ACETAMIDE (p. 6).

CHLORACETIC ACIDS. Two of these compounds are known, viz. *mono-* and *tri*-chloracetic acids, both being produced by the action of chlorine gas on glacial acetic acid under the influence of light, the former when the acid is in excess, the latter when the chlorine and the acetic acid are brought together in the exact proportions required for its formation. The trichlorinated acid is likewise produced in several other reactions. *Di*chloracetic acid has not yet been obtained, at least in definite form.

Monochloracetic Acid, or simply **Chloracetic Acid.** $C^2H^3ClO = C^2H^2ClO.H.O.$ (R. Hoffmann, Ann. Ch. Pharm. cii. 1.)—Dumas had observed that, in the preparation of trichloracetic acid by the action of chlorine on acetic acid in sunshine, a lower substitution-product is always obtained, especially if the acetic acid is in excess, in the form of an uncrystallisable acid, which however he did not succeed in preparing in the separate state. F. Leblanc afterwards obtained this acid, the monochloracetic acid, in the form of a colourless liquid, by passing chlorine through glacial acetic acid in the shade; his product however was not quite pure. More recently Hoffmann has shown that the chief product of the action of chlorine on excess of acetic acid in sunshine, is monochloracetic acid, and that this acid, when pure, is solid and crystalline at ordinary temperatures.

Preparation.—1. A tubulated retort of about 1 litre capacity and containing from half a pound to a pound of glacial acetic acid, is placed in a bath containing a saturated solution of nitrate of sodium (boiling at 120° C.), and dry chlorine gas is passed into the retort by a tube inserted through the tubulure and terminating just above the liquid, so that the gas may mix immediately with the vapour of the acid. The neck of the retort having a wide glass tube attached to it, is directed upwards, so that any acetic acid which evaporates undecomposed may be condensed and flow back again, while the hydrochloric acid and excess of chlorine escape. The whole apparatus is placed in the sunshine, and the evolution of chlorine is so regulated that the upper part of the retort always appears coloured by it. The stronger the light, the more rapid is the absorption of chlorine; but the action takes place, though slowly, even under a clouded sky. A very slow substitution of chlorine for hydrogen likewise takes place in the dark and at ordinary temperatures. As the formation of chloracetic acid goes on, the action slackens, so that it is best, after about fifteen hours' exposure to sunshine, or twice as long to diffused daylight, to expel the excess of chlorine from the apparatus by a steam of dry air, and rectify the product in a smaller retort. The portion which distils below 130° C. consists almost wholly of unaltered acetic acid, and may be used in a subsequent preparation. That which passes over between 130° and 190° is easily separated, by repeated rectification, into acetic and a thick liquid which boils between 185° and 187°, and either solidfies immediately into a mass of white needle-shaped crystals, or yields after some time, large, isolated, transparent, colourless rhombic tables, while the greater portion remains liquid, but if shaken up or stirred with a glass rod, solidifies suddenly and with considerable rise of temperature, the crystals previously formed becoming opaque and white like porcelain. The crystalline mass, which melts between 45° and 47°, consists of nearly pure monochloracetic acid, mixed however with a certain quantity of liquid, which may be removed by decantation and rapid pressure, and used, together with the portion of the original liquid which distilled below 130°, in a subsequent preparation. The expressed crystals are placed on bibulous paper and completely dried in vacuo over oil of vitriol and a few lumps of hydrate of potassium, and then redistilled, the first and last portions of the distillate being rejected. As they are very deliquescent, they should be kept as much as possible from the air. (Hoffmann.)

In the first distillation and in the subsequent rectifications, there is obtained a small quantity of a liquid which boils above 190°, and appears to contain an acetic acid with more than 1 at. hydrogen replaced by chlorine. It yielded in different experiments from 48 to 50 per cent. of chlorine, which does not agree with the formula either of dichloracetic (requiring 55·04) or of trichloracetic acid (requiring 65·13 per cent. of chlorine). In one experiment, this liquid, on being saturated with baryta, yielded, besides monochloracetate of barium, a small quantity of small, opaque, warty crystals, the composition of which seemed to show that they contained a higher chlorinated acid; but in no instance, even when the purest crystallised acetic acid was used and the absorption took place in the brightest sunshine, was any definite dichloracetic or trichloracetic obtained, the chief product being invariably monochloracetic acid. Neither was any oxalic acid formed, as in Dumas' preparation of trichloracetic acid (p. 877). (Hoffmann.)

2. Monochloracetic acid is also obtained in a state of purity by the action of water on monochlorinated chloride of acetyl. On distilling the liquid, the thermometer rises from 100° to 180°, and the liquid which passes over at that temperature solidifies in a crystalline mass on cooling. (Wurtz.)

Properties.—The acid crystallises from fusion in rhombic tables, having acute angles of 77° or 78°; from solution in acetic acid—*e.g.* from the liquids obtained in the first distillation between 180° and 186°, and between 186° and 190°—in crystals having a prismatic character, and very much resembling those of trichloracetic acid. Melting point 62°. It contracts strongly in solidifying, and generally gives off numerous air-bubbles. The specific gravity of the melted acid at 73°, is 1·366 as compared with water at 19°, and 1·3947 compared with water at 73°. Boiling point from 185° to 187·8°. It distils undecomposed, and when pure solidifies in the neck of the retort; but if mixed with acetic acid, remains liquid below its ordinary point of solidification. When kept for some time at a temperature near its melting point, it sublimes in long spicular crystals. It is nearly inodorous at ordinary temperatures, but its vapour has a pungent suffocating odour. It has a strong acid taste, attacks the cuticle, and raises blisters if kept on it for some time. It deliquesces in the air, and dissolves very easily in *water*, producing considerable fall of temperature.

Decompositions.—1. The acid is decomposed by *pentachloride of phosphorus*, with formation of oxychloride of phosphorus and monochlorinated chloride of acetyl, but the two chlorides cannot be separated by distillation, as they both boil at about 110°. When the product was repeatedly distilled with small portions of acid chloracetate of potassium, the residues of the last distillations yielded at high temperatures a large proportion of chloracetic acid, the last portions of which boiled as high as 200°, and had a more penetrating odour, probably arising from the presence of a small quantity of the anhydrous acid.—2. The acid heated with *potash-ley*, *ammonia*, *baryta-water*, or *lime-water*, immediately yields a chloride of the alkali-metal and glycollic acid. (Kekulé.)

$$C^2H^2ClMO^2 + H^2O = MCl + C^2H^4O^3.$$

3. Chloracetic acid is reduced by *potassium-amalgam* or *sodium-amalgam* to acetic acid, in the same manner as trichloracetic acid; the decomposition is however incomplete, and is attended with evolution of hydrogen. (Hoffmann.)

The CHLORACETATES, $C^2H^2ClMO^2$, are obtained by digesting the oxides or carbonates in the aqueous acid: they are for the most part easily soluble and crystallisable.

Chloracetate of Ammonium decomposes by evaporation like the potassium-salt. It is more soluble than that salt, and solidifies only from a perfectly viscid solution, in the form of a crystalline cake, which deliquesces on exposure to the air.

Chloracetate of Barium. $C^2H^2ClBaO^2 + H^2O$.—May be obtained, even with very small quantities of material, in distinct prismatic crystals, apparently belonging to the trimetric system, and containing 39·99 per cent. barium (by calculation 40·06). Decomposes but little during evaporation, and separates out almost completely on cooling from a hot saturated solution. (Hoffmann.)

Chloracetate of Potassium. *a. Neutral.* $2C^2H^2ClKO^2 + 3H^2O$.—Obtained by saturating the acid with carbonate of potassium and evaporating to a syrup in vacuo over oil of vitriol. It then separates in thin colourless laminæ, which may be obtained pure by draining on bibulous paper. It is not deliquescent, and does not give up its water of crystallisation at 100° C., but is decomposed at a higher temperature, yielding chloride of potassium, glycollic acid, and a small quantity of glycolide, $C^2H^2O^2$. (Kekulé, Ann. Ch. Pharm. cv. 288):

$$C^2H^2ClKO^2 = KCl + C^2H^2O^2.$$

It is also decomposed when its solution is evaporated at a gentle heat. It is very soluble in water. After drying in vacuo, it yielded 24·63 per cent. potassium (by calculation, 24·55).

b. Acid. $C^2H^2ClKO^2.C^2H^3ClO^2$.—When a solution of the neutral salt is mixed with as much acid as it already contains, the whole solidifies to a thick pulp of small white pearly crystals, which may be purified by draining on bibulous paper or by drying over oil of vitriol. Sparingly soluble in water.

Chloracetate of Silver. $C^2H^2ClAgO^2$.—A hot solution of the acid saturated with oxide of silver, yields the salt on cooling in splendid rhomboïdal, iridescent laminæ (Wurtz).—Anhydrous. Dissolves sparingly in cold, more readily in hot water, and is easily obtained by cooling, in small nacreous scales, which blacken on exposure to light, and yield chloride of silver. Between 110° and 120° C. it decomposes with a kind of explosion, emitting the same odour as the acid when it evaporates, and leaving chloride of silver, mixed with a very small quantity of metallic silver.

Chloracetate of Ethyl. $C^4H^7ClO^2 = C^2H^2ClO^2.C^2H^5$. (E. Willm, Ann. Ch. Phys. [3] xlix. 97.)—Obtained by the action of alcohol on monochlorinated chloride of acetyl:

$$C^2H^6O + C^2H^2Cl^2O = C^4H^7ClO^2 + HCl.$$

The action, which is very violent, must be moderated by cooling the vessel externally, and as soon as it is finished, the product may be washed with water, dehydrated by chloride of calcium and rectified.

Colourless liquid, having an ethereal odour and burning taste, heavier than water and insoluble in that liquid. Boils at 143°·5 C. when the barometer stands at 758° mm. Vapour-density 4·46.

The ether burns with a bright flame, green at the edges. It is decomposed by potash, into alcohol and chloracetic acid, which then suffers further decomposition, yielding chloride and acetate of potassium.

Trichloracetic Acid. $C^2HCl^3O^2 = C^2Cl^3O.H.O.$ (Dumas, J. Chim. méd. vi. 659; also Ann. Ch. Pharm. xxxii. 101; Ann. Ch. Phys. lxxiii. 75; Melsens, Ann. Ch. Phys. [3] x. 233; Malaguti, Ann. Ch. Phys. [3] xvi. 10; Kolbe, Ann. Ch. Pharm. liv. 182; Gm. ix. 209; Gerh. i. 749.)—This acid was discovered by Dumas in 1839. It is produced: 1. By the action of 6 at. dry chlorine gas on 1 at. glacial acetic acid in sunshine (Dumas):

$$C^2H^4O^2 + 6Cl = C^2HCl^3O^2 + 3HCl.$$

2. In the oxidation of soluble chloral by a mixture of hydrochloric acid and chlorate of potassium, and of chloral either soluble or insoluble, by fuming nitric acid (Kolbe):

$$C^2HCl^3O + O = C^2HCl^3O^2.$$

3. By the action of chlorine gas in sunshine on dichloride of carbon covered with a layer of water (Kolbe):

$$C^2Cl^4 + 2H^2O + Cl^2 = C^2HCl^3O^2 + 3HCl;$$

part of the C^2Cl^4 is at the same time converted into C^2Cl^6.—4. In the decomposition of chloride of trichloracetyl (chloraldehyde) by water (Malaguti):

$$C^2Cl^4O + H^2O = C^2HCl^3O^2 + HCl.$$

5. In the decomposition of perchlorinated formic ether by water (Cloez, Ann. Ch Phys. [3] xvii. 300):

$$C^3Cl^6O^2 + 2H^2O = C^2HCl^3O^2 + CO^2 + 3HCl.$$

Preparation.—1. When glacial acetic acid is exposed to the sun in bottles of 5 or 6 litres capacity (in the proportion of 0·8 or 0·9 grms. of the acid to 1 litre of chlorine) crystals of trichloracetic acid make their appearance in about a day, together with a small quantity of oxalic acid. On opening the bottles, a mixture of hydrochloric acid gas with a small quantity of carbonic acid and a suffocating vapour, escapes with force. The bottles are then left open for some hours, till the gaseous mixture is completely expelled, and washed out with a small quantity of water, whereby a concentrated solution of trichloracetic acid is obtained, mixed, however, with hydrochloric acid, undecomposed acetic acid, and oxalic acid. When this solution is evaporated in vacuo over oil of vitriol and hydrate of potassium, water, hydrochloric acid, and part of the acetic acid escape, and the solution then yields crystals, first of oxalic, afterwards of trichloracetic acid. The mother-liquor distilled with phosphoric anhydride, which decomposes the oxalic acid, yields a distillate of acetic acid, and then, on changing the receiver, of trichloracetic acid, which soon solidifies to a crystalline mass. Lastly, the crystals are left for some hours in vacuo on several sheets of white blotting paper, so that the admixed acetic acid may soak into the paper. (Dumas.)

2. Insoluble chloral is treated with fuming nitric acid, and the action, which is at first attended with evolution of heat and abundant evolution of red fumes, is afterwards assisted by the application of a gentle heat, till the flakes of insoluble chloral have completely disappeared; the greater part of the excess of nitric acid is then distilled off;

and the remaining portion is left to evaporate in vacuo over oil of vitriol and hydrate of potassium. Crystallised trichloracetic acid then remains, free from nitric, acetic, and oxalic acid, but generally retaining traces of chloral. (Kolbe.)

3. When dichloride of carbon, C^2Cl^4, is placed in a bottle filled with chlorine gas, covered with a film of water, and exposed to the sun, there is formed, besides C^2Cl^6, an aqueous solution of trichloracetic acid, which may be obtained in the crystalline state by evaporation in vacuo over oil of vitriol and lime. (Kolbe.)

4. Chloraldehyde is dissolved in water; and the solution containing hydrochloric acid is evaporated in vacuo over oil of vitriol and hydrate of potassium, whereby trichloracetic acid is obtained in beautiful crystals. (Malaguti.)

Properties.—Trichloracetic acid forms colourless rhombohedrons. It melts above 46° C., and in cooling begins to solidify at 45°; if the mass be then shaken, the temperature rises to 46°, which is therefore the melting point. In the fused state, it has a density of 1·617 at 46°, that of water at 15° being 1·000. Boils between 195° and 200° without any decomposition, and sublimes in the form of a silvery crust. Vapour-density = 5·3, by calculation 5·637, the difference arising from partial decomposition. The acid has a faint odour at ordinary temperatures, but when heated till it volatilises, it emits a pungent and suffocating odour. It has a caustic, sour taste, and makes the tongue white, like peroxide of hydrogen. It destroys the cuticle, causing it to peel off on the following day, and if left for some time on the skin, produces blisters. It reddens litmus strongly, but does not bleach it, even after a considerable time. It deliquesces in the air and dissolves readily in water. (Dumas.)

Decompositions.—1. When the acid is heated with *strong sulphuric acid*, part of it distils over unchanged, and crystallises in rhombohedrons; the rest is resolved into hydrochloric acid, carbonic anhydride, and carbonic oxide (Dumas). [Perhaps in this manner: $C^2HCl^3O^2 + H^2O = 3HCl + CO + CO^2$].—2. When it is heated with excess of *potash-solution*, ebullition takes place, continuing after the vessel has been removed from the fire; the first products of the action are chloroform and carbonate of potassium; but on further boiling with the alkaline liquid, the chloroform is resolved into formate and chloride of potassium. (Dumas.)—First:

$$C^2HCl^3O^2 + K^2O = CHCl^3 + K^2CO^3$$

then:

$$CHCl^3 + 2K^2O = CHKO^2 + 3KCl.$$

When the acid is boiled with baryta-water, carbonate of barium is precipitated and chloroform evolved (Dumas).—3. The acid boiled with excess of *ammonia*, is resolved into carbonate of ammonium, which sublimes, and chloroform, which sinks down as an oil (Dumas):

$$C^2HCl^3O^2 + (NH^4)^2O = (NH^4)^2.CO^3 + CHCl^3.$$

4. Aqueous trichloracetic acid, or either of its salts dissolved in water, is decomposed by *potassium-amalgam* (1 pt. potassium to 150 pts. mercury) with evolution of heat, and reconverted into acetate of potassium (Melsens). If the amalgam is not in excess in proportion to the acid, no hydrogen is evolved. Antimonide of potassium, or potassium alone, or zinc with sulphuric acid, does not effect the transformation, but causes an evolution of hydrogen gas (Melsens).—If instead of 6 at. potassium, only 3 at. be used in the form of potassium-amalgam, no acetic acid is produced, but apparently an acid containing a smaller quantity of chlorine than trichloracetic acid. 5. *Zinc* dissolves in aqueous trichloracetic acid, and forms, besides chloride of zinc, a zinc-salt which appears to contain dichloracetic acid $C^2Cl^2H^2O^2$. Trichloracetic acid is also reduced to acetic acid in the galvanic circuit of a two-pair Bunsen's zinc-carbon battery, with electrodes of amalgamated zinc. (Kolbe.)

TRICHLORACETATES.—Trichloracetic acid is monobasic, like acetic acid, the formula of its salts being $C^2MCl^3O^2$.

Trichloracetate of Ammonium. $C^2(NH^4)Cl^3O^2 + 2H^2O$.—The aqueous acid saturated with ammonia, and evaporated at ordinary temperatures, either in vacuo or in the air, yields crystals (Dumas). The salt is likewise produced when trichloracetamide is brought in contact with aqueous ammonia or very dilute nitric acid (Malaguti, Cloez). It crystallises in beautiful prisms (containing 2 at. water, melts at 80°; boils between 110° and 115° C., giving off vapours of chloroform and acid carbonate of ammonium, the latter appearing in peculiar abundance at 145°; and solidifies at 160° in yellowish, micaceous scales of anhydrous trichloracetate of ammonium, which are tasteless, dissolve readily in water, and give off ammonia when treated with potash, even in the cold. At a higher temperature, these scales fuse, and are resolved into carbonic oxide, phosgene, and sal-ammoniac vapour. (Malaguti.)

Decomposition of the crystallised salt:

$$C^2(NH^4)Cl^3O^2 + 2H^2O = CHCl^3 + NH^4.H.CO^3 + H^2O.$$

Decomposition of the anhydrous salt:

$$C^2(NH^4)Cl^3O^2 = CO + CCl^2O + NH^4Cl.$$

Trichloracetate of Potassium. $2C^2KCl^3O^2 + H^2O$.—The aqueous acid neutralised with carbonate of potassium yields by spontaneous evaporation, silky needles, which decompose with a kind of detonation when gently heated, and absorb only a small quantity of water when exposed to damp air. (Dumas.)

The *Barium* and *Calcium salts* are neutral and dissolve very readily in water. (Dumas.)

Trichloracetate of Silver. $C^2AgCl^3O^2$.—Recently precipitated oxide of silver immersed in the aqueous acid is converted into grey laminæ which dissolve in a larger quantity of water, and crystallise therefrom by evaporation in vacuo over oil of vitriol and in the dark, in crystalline granules and laminæ. The salt is very readily decomposed by light. When heated on a sheet of paper, it detonates violently, giving off the same odour as trichloracetic acid when it evaporates, and leaves vegetations of pure chloride of silver. If it be moistened with alcohol and the alcohol set on fire, it decomposes more quietly, and without projection. (Dumas.)

Trichloracetate of Ethyl. Trichloracetic Ether. $C^2Cl^3O^2.C^2H^5$.—Obtained either by distilling trichloracetic acid with alcohol and a small quantity of sulphuric acid (Dumas), or by gradually adding chloraldehyde to alcohol. (Malaguti.)

$$\underset{\text{Chloral-dehyde.}}{C^2Cl^4O} + C^2H^6O = C^2Cl^3O^2.C^2H^5 + HCl.$$

The product obtained by either of these processes is precipitated by water, washed with water, and dried over chloride of calcium. It is a colourless oil, smelling like peppermint. Specific gravity 1·367. Boiling point 164°. Vapour-density 6·64.

Aqueous *potash* decomposes it, forming alcohol and trichloracetate of potassium:

$$C^2Cl^3O^2.C^2H^5 + KHO = C^2H^6O + C^2Cl^3KO^2.$$

Ammonia converts into trichloracetamide, $N.H^2.C^2Cl^3O$ (p. 22).

Exposed to the action of chlorine in daylight, and in direct sunshine, it yields the same products as acetate of ethyl (p. 22). It is isomeric with the compound obtained by passing dry chlorine through dichloracetic ether contained in a vessel, the upper part of which is protected from the light. The two compounds are distinguished from each other by their behaviour with potash, the latter yielding, not trichloracetate of potassium, but chloride of potassium, deliquescent chlorinated potassium-salts, and a sweet oily liquid no longer decomposible by potash. (Leblanc.)

The higher chlorinated compounds produced by the action of chlorine on acetate of ethyl may be regarded as compounds of trichloracetic acid with ethyl in which the hydrogen is more or less replaced by chlorine: thus tetrachloracetic ether $C^4H^4Cl^4O^2 = C^2Cl^3O^2.C^2H^4Cl$; perchloracetic ether, $C^4Cl^8O^2 = C^2Cl^3O^2.C^2Cl^5$. All these compounds, indeed, when treated with potash, yield trichloracetate of potassium, *e.g.*:

$$C^4Cl^8O^2 + 2KHO = 2C^2Cl^3KO^2 + 2HCl.$$

Some of them however appear to be susceptible of isomeric modifications.

Trichloracetate of Methyl. $C^2Cl^3O^2.CH^3$.—Obtained by processes exactly similar to those which yield the ethyl-compound, viz. by distilling the acid with wood-spirit and sulphuric acid, or by the action of wood-spirit on chloraldehyde. It is a colourless oil, heavier than water, and smelling like peppermint. It is isomeric with the compound $C^3H^3Cl^3O^2$, obtained by the action of chlorine on acetate of methyl. The two compounds are not however identical; for the former is converted by potash into methyl-alcohol and trichloracetate of potassium (together with formate and chloride of potassium resulting from the further action of the potash, p. 45); the latter when treated with potash yields chloride and formate of potassium, together with chloromethylase, $CHCl$. (Laurent, see p. 23.)

Trichloracetate of methyl exposed to the action of chlorine in sunshine, is converted into perchloromethylic acetate, $C^3Cl^6O^2$, a compound also produced by the continued action of chlorine on acetate of methyl.

CHLORACETONES. See ACETONE (p. 29).

CHLORACETONITRILE. See ACETONITRILE (p. 33).

CHLORACETYL. C^2H^2ClO.—The radicle of chloracetic acid, chloracetamide, &c.

Trichloracetyl, C^2Cl^3O, is the radicle of trichloracetic acid, trichloracetamide, chloral, chloraldehyde, chloralide, &c.

CHLORACETYPHIDE. *Trichloracephosphide. Phosphide of Trichloracetyl and Hydrogen.* $C^2H^2Cl^3PO = P.H^2.C^2Cl^3O$.—This compound, the analogue of trichloracetamide, is produced by the action of chloride of trichloracetyl on phosphoretted hydrogen:

$$C^2Cl^3O.Cl + PH^3 = HCl + P.H^2.C^2Cl^3O,$$

also, together with oxychloride of carbon, when phosphoretted hydrogen is passed into heated perchloroformic ether:

$$C^3Cl^6O^2 + PH^3 = P.H^2.C^2Cl^3O + COCl^2 + HCl.$$

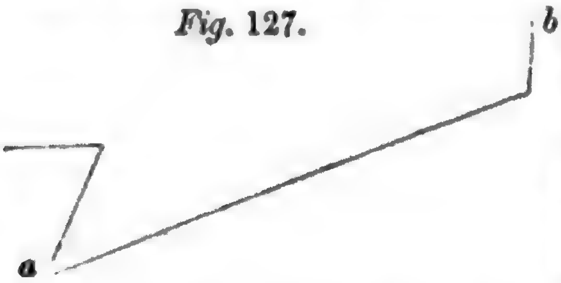
It forms small, white, crystalline scales, having a slightly alliaceous odour and bitter taste. It is permanent in the air at ordinary temperatures, but decomposes when heated, leaving a carbonaceous residue containing phosphoric acid. It is insoluble in water; slightly soluble in alcohol, ether, and wood-spirit. (Cloez, Ann. Ch. Phys. [3] xvii. 309.)

CHLORAL. *Hydride of Trichloracetyl.* $C^2HCl^3O = C^2Cl^3O.H$.—This body was discovered by Liebig in 1832 (Ann. Ch. Pharm. i. 189), and further examined by Dumas (Ann. Ch. Phys. [2] lvi. 123) and Städeler (Ann. Ch. Pharm. lxi. 101). It is the ultimate product of the action of chlorine upon alcohol:

$$C^2H^6O + Cl^8 = C^2HCl^3O + 5HCl.$$

Probably the alcohol is first converted into aldehyde by abstraction of 2H; and in this compound 3H are afterwards replaced by 3Cl (see ALCOHOL). Choral cannot, however, be obtained by the direct action of chlorine on aldehyde; it appears to be produced in the first instance, but is quickly converted into other products. For the production of chloral from alcohol, it is absolutely necessary that the alcohol be anhydrous; if water is present, aldehyde, acetal, acetic acid, acetic ether, and other products are formed instead of chloral; these products also accompany the chloral, even when the preparation is made with absolute alcohol (see ALCOHOL, *Decomposition by Chlorine*, p. 74). Chloral is also produced by the action of chlorine on starch or sugar. (Städeler.)

Fig. 127.



Preparation.—1. From alcohol. Pure and dry chlorine gas is passed into absolute alcohol contained in a tubulated retort having its neck directed upwards, and fitted with a long condensing tube, which passes down to the bulb, and projects considerably above the extremity of the neck to carry off uncondensed gases; the chlorine is introduced through the tubulus. Or the alcohol may be contained in a tube bent, as shown in *fig.* 127, the middle portion being 2 or 3 ft. long, and placed at a slight inclination, so that the chlorine entering at the lower part, may pass through a column of alcohol of considerable length but no great height. The chlorine is best evolved from a mixture of common salt, peroxide of manganese and sulphuric acid (which gives it off more regularly than hydrochloric acid and manganese); it must be passed first through a wash-bottle containing water, and then through sulphuric acid or over chloride of calcium, to dry it. The unabsorbed chlorine, together with hydrochloric acid gas and vapour of hydrochloric ether, may be passed into two Woulfe's bottles, and thence into the open air, so that the operator may not be annoyed by it. At the commencement of the operation, the alcohol is cooled by affusion of cold water, to prevent it from taking fire and depositing soot; but afterwards, when the absorption of the chlorine diminishes, and the liquid assumes a yellow colour, it must be gradually heated, and at last nearly to the boiling point; 200 grammes of alcohol require the passage of a rapid stream of chlorine to be continued for 15 or 20 hours, involving a consumption of about 1200 litres of chlorine gas. The alcohol becomes continually thicker, acquires a higher boiling point, and is finally converted into a heavy syrup, which, after standing for some days, solidifies completely to a soft, white crystalline mass, consisting of hydrate of chloral, together with a small quantity of hydrochloric acid and undecomposed alcohol: *Crude Hydrate of Choral.* If a sample of the liquid, after being agitated with four times its volume of sulphuric acid, and set aside, does not in a few hours form a solid stratum of insoluble chloral above the oil of vitriol, the passage of the chlorine must be continued for a still longer time. The solidified crystalline mass is heated till it melts, briskly agitated with 4 to 6 times its bulk of sulphuric acid, which does not heat or blacken it; left at rest till the dehydrated chloral has risen to the top of the sulphuric acid, a result which may be accelerated by gentle heating; and the transparent, colourless film of chloral is immediately decanted by means of a pipette. If the sulphuric acid contains water, it is particularly necessary to decant as quickly as possible, before the chloral is thereby converted into insoluble chloral. Lastly, the chloral is distilled over lime which has been slaked and subsequently ignited, to remove hydrochloric acid, care being taken to keep the whole of the lime below the surface of the liquid, as it will otherwise decompose the vapour and become red-hot. In this manner the chloral is obtained tolerably pure; but it still contains traces of water and alcohol, which may be removed by repeated treatment with sulphuric acid, the chloral being each time rectified over lime. All these operations must be performed in well closed vessels. (Liebig.)

2. By distilling starch or sugar with hydrochloric acid and peroxide of manganese (Städeler). 1 pt. of starch, or grape-sugar, or common sugar, is gently heated with 7 pts. of commercial hydrochloric acid free from sulphurous acid and diluted with an equal volume of water, till the paste (formed when starch is used) has become fluid; the liquid, when cold, is introduced, together with 3 pts. of manganese and a small quantity of common salt (to fix the sulphuric acid produced from the sulphurous acid in the commercial hydrochloric acid) into a capacious flask, in which it is heated as quickly as possible to the boiling point; and the fire is then completely removed. The mass swells up, giving off a large quantity of carbonic acid, and continues to boil for some time by itself. As soon as the ebullition slackens, it must be kept up by fresh application of heat, and the distillate collected, as long as it becomes turbid when mixed with tolerably strong potash-ley (in consequence of separation of chloroform from the chloral). More hydrochloric acid is then repeatedly introduced into the flask by small portions, till the distillate no longer smells of chloral, or becomes turbid with potash. The watery distillate is carefully freed from the colourless oil-drops, heavier than water and smelling of chloroform, which are produced at the beginning of the distillation; and saturated with common salt, in order to raise its boiling point and retain the water. It is then redistilled, and the resulting distillate is freed from a sulphur-yellow very pungent oil, and distilled several times more with common salt, the oily drops being each time removed, in order to obtain aqueous chloral as concentrated as possible, and as free as possible from the yellow oil, which greatly impedes the purification.

The removal of this oil is facilitated by saturating the distillate, before each rectification, with chalk, which decomposes the oil, but does not attack the chloral. The concentrated solution of chloral is saturated with dry chloride of calcium, and distilled in an oil-bath at 120° C. Hydrate of chloral then passes over, as a colourless liquid, which solidifies in the receiver into a crystalline mass. The last portions of the distillate are contaminated with a brown oily substance. 1. From the hydrate of chloral thus obtained, the anhydrous chloral may be separated by distillation, and purified in the manner above described. (Städeler.)

Properties.—Chloral is a thin colourless oil, greasy to the touch, and making grease-spots on paper, which, however, soon disappear. Specific gravity = 1·502 at 18° C., 1·518 at 0°, 1·4903 at 22°. Boils at 94·4° (Liebig); at 98·6 when the barometer stands at 760 mm. (Kopp), and distils without decomposition. Vapour-density = 5·13. It has a peculiar pungent odour, and excites a copious flow of tears: its taste is greasy and slightly astringent. It acts very strongly on the skin, especially when its boiling vapour comes in contact therewith. It has no acid reaction, even when dissolved in water, and does not precipitate a solution of silver.

Mixed with a small quantity of water, it becomes heated and solidifies, forming a mass of crystals of *hydrate of choral*, $C^2HCl^3O.H^2O$: a larger quantity of water dissolves it, and the solution evaporated in vacuo deposits the hydrate of chloral in large rhombic laminæ. The hydrate volatilises gradually in the air, and distils without decomposition when heated. Its vapour-density is 2·76.

Chloral dissolves also in alcohol and in ether. It absorbs chlorine gas without further change, and readily dissolves iodine, bromine, sulphur, and phosphorus, especially when heated. The iodine-solution has a purple-colour.

Decompositions.—1. Chloral is under certain circumstances inclined to pass into an isomeric insoluble modification (p. 64).—2. Anhydrous chloral distils, for the most part unchanged, with *strong sulphuric acid;* but when hydrate of chloral is heated with that acid, part of the chloral distils over in the anhydrous state, while the rest is converted into *chloralide* (p. 61), with evolution of hydrochloric and sulphurous acids, and a trace of carbonic acid. This reaction serves for the detection of chloral in liquids. The liquid, concentrated by several distillations over chloride of calcium, is heated for some time, with six times its volume of strong sulphuric acid, to 125° C, and diluted, after cooling, with six measures of water. Chloralide then separates out mixed with carbonaceous particles; and the mixture washed, pressed between paper, exhausted with ether and evaporated, yields crystals of chloralide, which may be further purified by heating with sulphuric acid and recrystallisation from ether.—3. *Fuming nitric acid*, if ultimately aided by heat, converts chloral into trichloracetic acid: the same transformation is effected by a mixture of hydrochloric acid and chlorate of potassium.—4. *Anhydrous metallic oxides*, such as baryta, strontia, lime, cupric oxide, mercuric oxide, and peroxide of manganese, exert no action upon chloral, when that liquid is distilled over them. If, however, in the distillation of chloral over baryta, strontia or lime, a portion of the oxide is left dry, or if either of these substances is heated in chloral vapour merely to 100°, it becomes red-hot, and completely decomposes the choral, with evolution of carbonic oxide, and formation of a metallic chloride mixed with charcoal.—5. *Alkalis*, either in the form of solid hydrates or of aqueous solutions, decompose chloral readily at ordinary temperatures, with evolution of heat, converting it into formate of potassium and chloroform, and a portion of the latter compound is further decomposed, yielding formate and chloride of potassium:

$$\underset{\text{Chloral.}}{C^2HCl^3O} + KHO = \underset{\text{Formate of potassium.}}{CHKO^2} + \underset{\text{Chloroform.}}{CHCl^3}.$$

and $$CHCl^3 + 4KHO = CHKO^2 + 3KCl + 2H^2O.$$

—5. Vapour of chloral passed over *red-hot iron* yields carbonic oxide, and chloride of iron mixed with charcoal.—6. *Potassium*, in contact with chloral, eliminates hydrogen, and forms a resinous body from which water extracts potash and choride of potassium. —7. Chloral forms with *ammonia* a compound, which, like aldehyde-ammonia, reduces silver in the specular form, and from which sulphydric acid throws down a sulphuretted compound apparently analogous to thialdine (Städeler, Ann. Ch. Pharm. cvi. 253). — 8. *Sulphydric acid gas* passed through an aqueous solution of chloral separates a sparingly soluble crystalline compound, which is probably analogous to acetyl-mercaptan (p. 107), but decomposes much more easily, giving off sulphydric acid even during drying (Städeler). — 9. By boiling hydrate of chloral with *hydrocyanic* and *hydrochloric acid*, a syrupy acid is formed resembling lactic acid. These last three reactions indicate a close analogy between chloral and aldehyde, which is further strengthened by the fact that chloral forms crystalline compounds with acid sulphites of alkali-metal. (Städeler.)

Insoluble Chloral, Metachloral (Gm. viii. 205; Gerh. i. 671.) — Chloral is converted, under certain circumstances, into an isomeric modification insoluble in water. This change takes place spontaneously when chloral is preserved in a stoppered bottle, or when it is placed in contact with a quantity of water not sufficient to convert it into the hydrate. Metachloral thus prepared is pure, and has the same composition as chloral. It is also produced, mixed, however, with a little chloralide, by the action of sulphuric acid upon chloral. A layer of the crude hydrate of chloral obtained in the preparation of chloral from alcohol (p. 880), left in contact with strong sulphuric acid, solidifies in a few hours into a mass of insoluble chloral. Pure chloral in contact with six times its volume of strong sulphuric acid, undergoes the same transformation in the course of a night. The metachloral thus obtained may be purified from chloralide by pulverising, and washing it, first with water and then with alcohol.

Metachloral is a white powder, greasy to the touch, and having a faint aromatic odour. It volatilises slowly in the air or in vacuo. It is insoluble in water, alcohol, and ether. When perfectly dry, it is reconverted by heat into soluble chloral, at 180°C, according to Kolbe, above 200° according to Regnault. Heated with sulphuric acid, it partly distils over as soluble chloral, but a considerable portion is decomposed, with formation of chloralide, and evolution of hydrochloric and sulphurous acids. By fuming nitric acid, metachloral is, like chloral, converted into trichloracetic acid; but it is not attacked by a mixture of hydrochloric acid and chlorate of potassium. With solutions of the caustic alkalis, it behaves like ordinary chloral, yielding an alkaline formate and chloroform; but the quantity of the latter is less as the alkali is more concentrated.

CHLORAL, AMYLIC. See CHLORAMYLAL.

CHLORAL, MESITIC. This name was applied by Kane (Pogg. Ann. xliv. 473) to a pungent vesicating liquid of specific gravity 1·33, and boiling at 71° C., which is obtained by passing dry chlorine into acetone. Kane's analysis gives 56·8 per cent. chlorine; Liebig found only 52·6 per cent. It is probably a mixture containing two or more of the chloracetones (p. 29).

CHLORAL, PROPIONIC. *Hydride of Pentachloropropione*, $C^3Cl^5O^2.H$. This body is found amongst the products obtained by distilling starch with a mixture of hydrochloric acid and peroxide of manganese. On saturating the acid distillate with chalk or carbonate of sodium, and rectifying over a small quantity of chloride of calcium, the propionic chloral passes over among the first portions, together with an oil. To remove the latter, the rectified distillate is agitated several times with ice-cold water, and the cold saturated solution is decanted and heated, the propionic chloral then separating in heavy drops having a faint yellow colour. By diffusing these drops through a small quantity of water, and exposing them to a temperature of 0° C., colourless tables are obtained, which may be purified from adhering oil by pressure between bibulous paper. They consist of a hydrate containing 4 at. water: $C^3HCl^5O^2.4H^2O$. (Städeler, Handw. d. Chem. Suppl. ii. 796.)

CHLORALBIN. $C^6H^6Cl^2$.—A crystalline substance contained in trichlorophenic acid prepared by passing chlorine through coal-tar. It is separated by treating the crude acid with ammonia and alcohol, or better with ether, whereupon the chloralbin remains in very white needles; it may be further purified by dissolving it in boiling ether. It is but sparingly soluble in boiling alcohol, and insoluble in alkalis. It boils at 190° C., and crystallises on cooling in fern-like tufts. At a higher temperature, it sublimes without alteration and crystallises in needles. It is not attacked by hot nitric or sulphuric acid. (Laurent, Rev. scient. vi. 72.)

CHLORALDEHYDES. These compounds are aldehydes in which the hydrogen is more or less replaced by chlorine, and may be regarded as derived from the corresponding acids by the substitution of 1 or more at. chlorine for an equivalent quantity of peroxide of hydrogen HO, thus:

	Chloraldehydes.	Acids.
Acetic	$C^2H^3O.Cl$	$C^2H^3O.HO$
Trichloracetic . . .	$C^2Cl^3O.Cl$	$C^2Cl^3O.HO$
Nitric	$NO^2.Cl$	$NO^2.HO$
Sulphuric	$(SO^2)''.Cl^2$	$(SO^2)''.(HO)^2$
Phosphoric	$(PO)'''.Cl^3$	$(PO)'''.(HO)^3$

The chloraldehydes are a more numerous class of compounds than the aldehydes themselves, including many compounds usually denominated oxychlorides, *e. g.* oxychloride of phosphorus. They bear to their corresponding acids the same relation that metallic chlorides bear to metallic hydrates.

The term chloraldehyde is also specially applied to the second compound in the above list, viz:

Chloride of Trichloracetyl or *Perchlorinated Acetic Aldehyde*, $C^2Cl^4O = C^2Cl^3O.Cl$.—This body, discovered by Malaguti (Ann. Ch. Phys. i. [2] xvi. 5); Gm. ix. 218; Gerh. i. 756), is a constant product of the action of heat on the perchlorinated ethylic (vinic) ethers. Thus:

$$\underset{\text{Perchlor. oxide of ethyl.}}{C^4Cl^{10}O} = C^7Cl^4O + \underset{\text{Sesquichloride of carbon.}}{C^2Cl^6}.$$

$$\underset{\text{Perchlor. formate of ethyl.}}{C^3Cl^6O^2} = C^2Cl^4O + \underset{\text{Oxychloride of carbon.}}{COCl^2}.$$

$$\underset{\text{Perchlor. acetate of ethyl.}}{C^4Cl^8O^2} = 2C^2Cl^4O$$

$$\underset{\text{Perchlor. carbonate of ethyl.}}{C^5Cl^{10}O^3} = C^2Cl^4O + C^2Cl^6 + CO^2.$$

$$\underset{\text{Perchlor. oxalate of ethyl.}}{C^6Cl^{10}O^4} = 2C^2Cl^4O + COCl^2 + CO.$$

It is best prepared from perchlorinated oxide of ethyl, $C^4Cl^{10}O$ (the product obtained by the continued action of chlorine in sunshine, on anhydrous ether). This compound is resolved at 300° C. into chloride of trichloracetyl and trichloride of carbon; and by subjecting the mixture to repeated fractional distillation, the trichloride of carbon is left behind, and the chloride of trichloracetyl is obtained pure. The rectification must be continued till the distillate no longer shows any turbidity when mixed with water.

Chloraldehyde is a transparent, colourless liquid, of specific gravity 1·603 at 18° C. Boiling point 118°. Vapour-density 6·32 (calc. 2 vol. 6·295). It gives off excessively pungent vapours on exposure to the air, and when placed on the tongue, first excites a sensation of dryness, then forms a white spot, and ultimately exerts a caustic action. It reddens litmus after a few seconds.

It sinks in water, and gradually dissolves, forming a clear solution of hydrochloric and trichloracetic acids: the same decomposition is produced by aqueous solutions of the fixed alkalis:

$$C^2Cl^3O.Cl + H^2O = HCl + C^2Cl^3O.H.O.$$

When a small quantity of alcohol is poured upon it, great heat is evolved, and the whole is quickly volatilised; but if the chloraldehyde be slowly added to an excess of alcohol, gradual decomposition takes place, attended with but little rise of temperature, the products being hydrochloric acid and trichloracetate of ethyl:

$$C^2Cl^3O.Cl + C^2H^5.H.O = HCl + C^2Cl^3O.C^2H^5.O$$

With ammonia it forms trichloracetamide (p. 22);

$$C^2Cl^3O.Cl + 2NH^3 = N.H^2.C^2Cl^3O + NH^4Cl,$$

and with phosphoretted hydrogen, PH^3, the analogous compound, chloracetyphide, $P.H^2.C^2Cl^3O$ (p. 879).

CHLORALIDE. $C^5H^2Cl^6O^3$. (Städeler, Ann. Ch. Pharm. lxi. 104.—Kekulé, *ibid.* cv. 293.)—A crystalline compound obtained by the action of sulphuric acid upon hydrate of chloral. To prepare it, hydrate of chloral is gently heated with 4 to 6 times its volume of strong sulphuric acid, the mixture being well shaken, and then distilled at a heat between 120° and 130° C., as long as unaltered choral continues to pass over. This choral is reconverted into hydrate by addition of a little water, then poured back, and the distillation is repeated till the greater part of the chloral is decomposed. The sulphuric acid is then found to be covered with a colourless oily liquid, which solidifies on cooling into a white crystalline crust. This mass is broken up, the sulphuric acid is drained off, and the crystals are washed with water, till the wash-water no longer reddens litmus; they are then dried between bibulous paper, and dissolved in ether, and the ethereal solution is mixed with ⅓ its volume of alcohol. The chloralide then separates as the ether evaporates, in well-defined crystals, which must be crystallised several times from a mixture of alcohol and ether, in order to free them from an oily matter which adheres to them:—According to Kekulé (Ann. Ch. Pharm. cv. 293), a purer and more abundant product is obtained by the action of fuming sulphuric acid on hydrate of chloral. When chloral which has been once distilled over ordinary sulphuric acid, is mixed with an equal volume of acid, a large quantity of hydrochloric acid is evolved, and about one-third of the chloral is converted into chloralide. Carbonic oxide is also given off abundantly, together with a very small quantity of carbonic anhydride; sulphurous anhydride occurs only towards the end of the process. The oily distillate solidifies on cooling in a crystalline mass, which may be purified by recrystallisation from boiling alcohol.

Kekulé explains the formation of chloralide and the accompanying products by the following equation:—

$$3C^2HCl^3O + H^2O = C^5H^2Cl^6O^3 + 3HCl + CO.$$

Städeler, on the other hand, considers it improbable that the conversion of the chloral into chloralide can be due to the action of water, inasmuch as fuming sulphuric acid seems to act better than ordinary sulphuric acid. He supposes that a triple molecule of chloral (insoluble chloral) splits up into chloralide and chloroform, according to the equation:

$$3C^2HCl^3O = C^5H^2Cl^6O^3 + CHCl^3,$$

and attributes the evolution of carbonic oxide observed by Kekulé, to the resolution of a molecule of chloral into this gas and chloroform:

$$C^2HCl^3O = CO + CHCl^3.$$

Chloralide is insoluble in water, and likewise in sulphuric acid. It dissolves sparingly in cold alcohol, but easily in boiling alcohol and in ether. From a hot saturated alcoholic solution, it is deposited in very delicate white needles; from a mixture of alcohol and ether, in stellate groups of rectangular prisms belonging to the monoclinic system, with oblique terminal faces, and generally having their lateral edges truncated. They are transparent and colourless, with a glassy lustre, and cleave with facility in a direction parallel to the prismatic faces. Chloralide melts between 112° and 114° C. to an oily liquid, emitting at the same time an odour like that of chloral: it solidifies at 108° (Kekulé). Chloralide burns at 200° (Städeler); at 260° (Kekulé) with a bright flame, green at the edges.

The alcoholic solution of chloralide does not precipitate nitrate of silver, but on adding a drop of ammonia, a precipitate is immediately formed, consisting of chloride of silver. Chloralide immersed in aqueous potash, is resolved into chloroform and formate of potassium; but if alcoholic solutions are used, the only products are formate and chloride of potassium, these compounds being in fact produced by the action of alcoholic potash upon chloroform.

The composition of chloralide has been variously stated by different chemists. Städeler, who discovered it, assigned to it the formula $C^5H^2Cl^6O^3$, which is confirmed by the recent experiments of Kekulé. Gerhardt (*Traité*, i. 672) proposed the formula $C^8H^3Cl^7O^4$; Gmelin (*Handbook*. ix. 207) gave $C^8H^4Cl^{10}O^8$, and in the *Handwörterbuch der Chemie*, 2^te Aufl. i. 112, the formula $C^4HCl^3O^2$ is assigned to this compound.

The following table exhibits the calculated composition of chloralide, according to the preceding formulæ, as compared with the results of analysis:

	Calculation according to:				*Analysis:*	
	Städeler.	Gerhardt.	Gmelin.	Handw.	Städeler.	Kekulé.
	$C^5H^2Cl^6O^3$	$C^6H^3Cl^7O^4$	$C^8H^4Cl^{10}O^5$	$C^4HCl^3O^2$	*mean*	*mean*
C . . .	18·61	18·50	17·98	18·55	18·64	18·64
H . . .	0·62	0·77	0·39	0·75	0·77	0·72
Cl . . .	65·88	64·10	68·62	66·29	66·20	66·00
O . . .	14·89	16·63	12·44	14·98		
	100·00	100·00	100·00	100·00		

CHLORALOÏL. A product of the action of chlorine upon aloin (p. 148).

CHLORALURIC ACID. An acid produced, together with other substances, by the action of chlorous acid on uric acid. It crystallises in nacreous laminæ; forms crystallisable salts with barium and lead, and a curdy precipitate with silver-salts. It gave by analysis 27·3 per cent. C, 3·8 H, 28·1 N, and 11·4 Cl, numbers which are approximately represented by the formula $C^{14}H^{22}N^{12}Cl^2O^{11}$. (Schiel, Ann. Ch. Pharm. cxii. 78.)

CHLORAMYLAL. C^5H^9ClO (?) — A heavy liquid produced by the action of chlorine upon amylic alcohol (*q. v.*)

CHLORANIL. Syn. with PERCHLOROQUINONE, $C^6Cl^4O^2$. (See QUINONE.)

CHLORANILAMIC ACID. Syn. with DICHLOROQUINONAMIC ACID. (See QUINONIC ACID).

CHLORANILAMIDE. Syn. with DICHLOROQUINONAMIDE. (See QUINONIC ACID.)

CHLORANILAMMONE. Syn. with DICHLOROQUINONAMATE OF AMMONIUM.

CHLORANILIC ACID. Syn. with DICHLOROQUINONIC ACID. (See QUINONIC ACID.)

CHLORANILINE. Syn. with CHLOROPHENYLAMINE. (See PHENYLAMINE.)

CHLORANISIC ACID. See ANISIC ACID (p. 302).

CHLORASTROLITE. A mineral found on the shores of Isle Royale, Lake Superior, in small rounded water-worn pebbles which have come from the trap. It has a finely radiated or stellate structure, light bluish-green colour, and pearly lustre slightly chatoyant on the rounded sides. Specific gravity 3·180. Hardness 5·5—6. Analyses by Whitney:

SiO^2	Al^4O^6	Fe^4O^3	Ca^2O	Na^2O	K^2O	H^2O
36·99	25·49	6·48	19·90	3·70	0·40	7·22 = 101·18
37·41	24·25	6·76	21·68	4·88		5·77 = 100·25

These numbers lead to the formula —

$$3\left[\left(\begin{matrix}\frac{6}{7}Ca^2O\\ \frac{1}{7}Na^2O\end{matrix}\right)^2.SiO^2\right] + 2\left[\left(\begin{matrix}\frac{6}{7}Al^4O^6\\ \frac{1}{7}Fe^4O^3\end{matrix}\right)^2.3SiO^2\right] + 6H^2O.$$

which, if M = Ca, Na and $m = \frac{2}{3}$ (Al, Fe), may be reduced to that of an orthosilicate, $(M^4m^6)Si^3O^{12} + 2\,aq.$

The mineral gives off water when heated, and melts with intumescence before the blowpipe to a greyish blebby glass. With borax it forms a transparent glass tinged with iron; blue with cobalt solution. Dissolves in hydrochloric acid, with separation of flocculent silica. (Dana, ii. 315.)

CHLORATES. Chloric acid, $HClO^3$, is monobasic and forms but one class of salts, having the general formula $MClO^3$ or $M^2O.Cl^2O^5$. They are all soluble in water, and are resolved by heat into oxygen and a metallic chloride. (See CHLORIC ACID under CHLORINE, p. 910.)

CHLORATE OF ALUMINIUM is a deliquescent salt obtained by precipitating a solution of silico-fluoride of aluminium with an equivalent quantity of potassium, and evaporating the filtrate. (Berzelius.)

CHLORATE OF AMMONIUM is obtained by adding ammonia or the carbonate to chloric acid; by precipitating an earthy chlorate with carbonate of ammonium; or by adding finely divided chlorate of potassium by small portions to a solution of silico-fluoride of ammonium, and filtering. It crystallises in slender needles, has a pungent taste, explodes when heated, and sometimes, according to Mitscherlich, even at ordinary temperatures. Dissolves easily in water and in alcohol.

CHLORATE OF BARIUM, $BaClO^3$.—Prepared: 1. By saturating aqueous chloric acid with baryta-water or carbonate of barium. *a.* A hot solution of chlorate of potassium is precipitated with hydrofluosilicic acid in slight excess, and the filtrate is saturated with carbonate of barium, whereupon chlorate of barium dissolves, and a small quantity of silico-fluoride of barium remains behind. The filtered solution yields crystals of the chlorate by evaporation (Wheeler, Ann. Ch. Phys. [2] vii. 74). *b.* A solution of 27 pts. chlorate of sodium in 54 pts. water is mixed with a solution of 38 pts. tartaric acid in 38 pts. water; the mixture is thrown into double the quantity of absolute alcohol; and the liquid, after standing 24 hours, is filtered from the crystallised tartrate of sodium, then saturated with carbonate of barium, &c. (Duflos, N. Br. Arch. xxiii. 306.) *c.* Equivalent quantities of chlorate of potassium and acid tartrate of ammonium (122·6 pts. of the former to 167 of the latter) are dissolved in the smallest possible quantity of boiling water; the liquid, after the acid tartrate of potassium has crystallised out, is mixed with an equal quantity of alcohol; the filtrate decomposed by boiling with carbonate of barium, &c. (L. Thompson, Jahresber. f. Chem. 1847—8, p. 381.)

2. By passing chlorine into hot water in which baryta is partly suspended, partly dissolved. Chloride and chlorate of barium are then formed, the greater part of the chloride is suffered to crystallise out, and the rest is removed by adding phosphate of silver to the solution, in the exact quantity required. (Chenevix, Vauquelin, *Gmelin's Handbook*, ii. 161.)

Chlorate of barium forms hydrated prismatic crystals, $2BaClO^3 + H^2O$, belonging to the monoclinic system. Ratio of orthodiagonal, clinodiagonal, and principal axis = 0·882 : 1 : 1·07. Inclination of axes = 85° 30'; $\infty P : \infty P$ in the orthodiagonal section = 97°; $[P\infty] : [P\infty]$, in the clinodiagonal section = 79° 10'. Ordinary combination $\infty P . [P\infty] . -P\infty$; also without $-P\infty$; also with $\infty P\infty$ (Kopp, *Krystallographie*, p. 304), and less frequently with 0P (Rammelsberg, Pogg. Ann. xc. 16). The crystals are transparent and colourless, give off their water (4·72 per cent.) at 120° C., oxygen at 250°, and melt at a temperature above 400° (Wächter, Ann. Ch. Pharm. lii. 231; Souchay, *ibid.* cii. 381). The salt detonates powerfully with combustible bodies; produces a green flame when heated with sulphur (Duflos); and emits a bright flashing light with strong sulphuric acid (Chenevix). It dissolves easily in water, but is insoluble in alcohol. The anhydrous salt dissolves in 4·38 pts. of water at 0° C., in 2·70 pts. at 20°, in 1·92 pts. at 40°, in 1·29 pts. at 60°, in 1·02 pts. at 80°, and in 0·79 pts. at 100° (Kremers, Jaheresber. d. Chem. 1856, p. 274.) According to Hutstein (Arch. Pharm. [2] lxxvii. 137) it emits light on crystallising.

Chlorate of Calcium, $CaClO^3 + H^2O$.—Prepared like the barium-salt. Crystallises in deliquescent rhomboïdal prisms, easily soluble in water and alcohol. They contain 16·5 p.c. water, melt in their water of crystallisation when gently heated, and decompose at a higher temperature. (Gm. iii. 212.)

Chlorate of Cobalt, $CoClO^3 + 3H^2O$.—Crystallises in cubo-octahedrons. Decomposed by ignition into chlorine, oxygen, and a residue containing oxide and chloride of cobalt. (Wächter, Ann. Ch. Pharm lii. 233.)

Chlorate of Copper, $CuClO^3 + 3H^2O$.—A solution of cupric oxide in chloric acid yields green deliquescent octahedrons having a slight acid reaction, and soluble in alcohol. At 100° C. it gives off a few gas-bubbles, and at 260° suffers further decomposition, leaving a residue which is insoluble in water but soluble in acids, and appears to consist of a basic chlorate, inasmuch as its solution in nitric acid gives no precipitate with silver-salts (Wächter, *loc. cit.*) Cupric chlorate detonates with bright green flame on glowing coals, and is much used in pyrotechny for the production of green fire.

Chlorate of Lead, $2PbClO^3 + H^2O$.—Rhomboïdal prisms, which become dull and opaque by exposure to the air; soluble in water and alcohol but not deliquescent. When heated, they leave oxychloride of lead containing Pb^6Cl^4O. (Wächter.)

Chlorate of Lithium, $2LiClO^3 + H^2O$.—Radiated, very deliquescent mass, melting at 0° C., and giving off water at 140°, together with oxygen and small quantities of chlorine. Very soluble in alcohol. (Wächter.)

Chlorate of Magnesium, $MgClO^3 + 3H^2O$.—Crystalline crust, easily soluble in alcohol, melting at 40° C., and giving off its water at 120°; (Chenevix, Wächter.)

Chlorate of Manganese.—Colourless, known only in solution.

Chlorates of Mercury.—The *mercuric* salt is obtained by dissolving mercuric oxide in warm chloric acid (Vauquelin), or by heating mercuric oxide with successive portions of chlorine-water, filtering from mercuric oxychloride, and concentrating the filtrate; mercuric chloride then crystallises out, while the chlorate remains in solution (Braamcamp and Siqueira.) Mercuric chlorate forms small deliquescent needles, which redden litmus, taste like the chloride, and are resolved by heat into oxygen gas, mercurous chloride, calomel, and metallic mercury. The salt does not deflagrate on red-hot coals, but sets fire to sulphide of antimony at ordinary temperatures. (Gm. vi. 62.)

Mercurous Chlorate, $Hg^2O.ClO^5$ or $HhgClO^3$. — A solution of mercurous oxide in chloric acid yields the salt in beautiful prismatic crystals, which dissolve in water and in alcohol, and are resolved by heat into oxygen, metallic mercury, and calomel. (Wächter.)

CHLORATE OF NICKEL, $NiClO^3 + 3H^2O$, crystallises in regular octahedrons of a deep green colour, deliquescent and soluble in alcohol. When heated, they give off oxygen and chlorine, and leave a mixture of chloride and oxide of nickel; at a very strong red heat, however, nothing but oxide remains behind. (Wächter.)

CHLORATE OF POTASSIUM, $KClO^3$, or $KO.ClO^5$.—This salt is an important article of manufacture, being used in the preparation of lucifer matches and for other purposes in the arts. It is prepared, either by passing chlorine into solution of potash or carbonate of potassium, whereby chlorate and chloride of potassium are formed, which are separated by crystallisation, the chlorate being much the less soluble of the two; or by decomposing chlorate of calcium with sulphate or chloride of potassium.

1. A solution of 1 pt. hydrate of potassium in 3 pts. water is saturated with chlorine gas, whereby chloride and hypochlorite of potassium are produced, the liquid acquiring strong bleaching properties:

$$2KHO + Cl^2 = KClO + KCl + H^2O.$$

The liquid is then left to itself for a day, or heated for some time to the boiling point, whereby the hypochlorite is completely resolved into chloride and chlorate:

$$3KClO = 2KCl + KClO^3.$$

The ultimate result is to convert 6 at. hydrate of potassium, by the action of 6 at. chlorine, into 1 at. $KClO^3$ and 5 at. KCl. It has been found that if a solution of potash either stronger or weaker than that above mentioned be used, part of the chlorate produced is decomposed into free oxygen and chloride of potassium.

The solution, when left to itself, deposits the greater part of the chlorate of potassium in crystals, which may be purified from adhering chloride by recrystallisation. The mother-liquor yields by concentration an additional quantity of chlorate, which, however, is more contaminated with chloride, and requires a greater number of crystallisations to purify it. The test of purity is that the solution is not clouded by a drop of nitrate of silver.

Carbonate of potassium may be used for the preparation instead of caustic potash. In that case a considerable quantity of acid carbonate of potassium is formed in the early stage of the process, and crystallises on the sides of the vessels; but on continuing the passage of the chlorine, this salt is decomposed, with evolution of carbonic acid, the ultimate products being chlorate and chloride of potassium as before.

Carbonate of potassium may also be used in the solid form, being laid on shelves or trays in a chamber into which chlorine gas is introduced, just as in the manufacture of bleaching powder. When the absorption of the chlorine is complete, the product is dissolved in water, and the chlorate crystallises out, as above described.

2. Hypochlorite of calcium, or bleaching powder, the so-called "chloride of lime" is made into a "cream" with water, and submitted to continuous boiling or evaporation to dryness, whereby it is resolved into a mixture of chlorate and chloride of calcium (p. 910), a change the completion of which is indicated by the loss of bleaching properties in the mass. The residue, after evaporation, is treated with water, and chloride or sulphate of potassium is added, whereby the chlorate of calcium is decomposed, with production of chlorate of potassium and chloride or sulphate of calcium. The chlorate, amounting to about $\frac{1}{10}$ of the weight of chloride of lime employed, is separated from sulphate of calcium by the insolubility of the latter, or from chloride of calcium by crystallisation.

The process now generally employed consists in a modification of the last, in which the chloride of lime is formed in the same operation as the chlorate itself, instead of starting from a previously manufactured bleaching powder. Excess of chlorine is passed into a mixture of 300 pts. caustic lime and 154 of chloride of potassium with 100 water, the operation being performed in close leaden tanks, heated by steam and provided with agitators. A man-lid, through which the tank can be cleansed or repaired, and one or two wide tubes descending nearly to the bottom of the vessel, through which materials can be introduced, complete the arrangement. During the action, the temperature rises to about 200° F. After the completion of this operation, the liquid is filtered and evaporated nearly to dryness by steam heat; and the resulting mass is redissolved in hot water and set to crystallise.

The whole of the chloride of calcium remains in the mother-liquors, and the crystals of chlorate are rendered fit for the market by slight washing and draining. The reaction upon which this operation depends is represented by the following equation:

$$KCl + 3Ca^2O + 6Cl = KClO^3 + 6CaCl.$$

In this process, 154 pts. KCl give more than 200 pts. $KClO^3$, while, by the method of direct saturation, 115 pts. caustic potash yield only 30 pts. of that salt; at the same time, no by-product is formed except chloride of calcium. The crystallisable mother-liquors of this manufacture consist, within 1 or 2 per cent., entirely of this salt, and may be decomposed either by an addition of sulphate of potassium or of carbonate of sodium. In the former case, sulphate of calcium is precipitated, available in the manufacture of paper, while chloride of potassium remains in solution, and may be recovered by evaporation, to be employed in the preparation of fresh portions of chlorate: in the latter, carbonate of calcium, the "creta præcipitata" of the druggist, is precipitated, and is largely employed by the pharmaceutist and the perfumer. Nearly the whole of the waste liquors of the English manufacturer are converted into the latter product.

Carbonate instead of chloride of potassium may also be mixed with the quick lime: in that case, on treating the mixture with water, after it has been exposed to the action of chlorine, the whole of the lime remains as carbonate, while chloride and chlorate of potassium are dissolved. (Gm. iii. 59, *Ure's Dictionary of Arts, Manufactures and Mines*, i. 66.)

Properties.—Chlorate of potassium crystallises in anhydrous six-sided laminæ, more rarely in needles. The crystals belong to the monoclinic system. Ratio of orthodiagonal, clinodiagonal, and principal axis = 1·360 : 1 : 0·804. Inclination of axes = 70° 11′. Ordinary combination $\infty P . 0P . +P . +2P\infty$; also twin-crystals. Cleavage parallel to ∞P and $0P$.

Chlorate of potassium is but slightly soluble in cold water. The quantities dissolved by 100 pts. of water at different temperatures, as determined by Gay-Lussac, are given in the following table:

at 0° C.	3·3 pts.	at 49·06° C.	18·98 pts.
15·37°	6·03 „	74·39°	85·40 „
24·43°	8·44 „	104·78°	60·24 „
35·02°	12·05 „		

It is insoluble in absolute alcohol.

Chlorate of potassium is permanent in the air at ordinary temperatures, but is easily decomposed by heat, being at first resolved into chloride and perchlorate of potassium, with a small quantity of free oxygen: $2KClO^3 = KCl + KClO^4 + O^2$, while at a higher temperature the whole of the oxygen is given off (39·15 per cent. of its weight in all), and chloride of potassium remains.

The decomposition is greatly facilitated by mixing the chlorate with peroxide of manganese or oxide of copper, the whole of the oxygen of the chlorate being then given off at a low red heat without previous formation of perchlorate: such a mixture is very convenient for the evolution of oxygen. The metallic oxide does not undergo any alteration, appearing to act merely by dividing the particles of the chlorate and preventing them from fusing into a mass.

Chlorate of potassium is a powerful oxidising agent, and detonates violently when mixed with certain combustible bodies and struck or heated. Triturated in a mortar with *flowers of sulphur*, it produces a series of sharp detonations. A mixture of the salt with *sulphide of antimony* takes fire when triturated, sometimes with explosion. A small quantity of the chlorate mixed with *phosphorus* and struck with a hammer detonates with a loud report. These combustions are attended with great danger when large quantities are used.

Chlorate of potassium is decomposed by acids, with evolution of peroxide of chlorine, chlorous acid, or hypochlorous acid. With *strong sulphuric acid*, it is resolved into peroxide of chlorine, perchlorate, and acid sulphate of potassium:

$$3KClO^3 + 2H^2SO^4 = 2ClO^2 + KClO^4 + 2KHSO^4 + H^2O$$

The decomposition is attended with violent decrepitation, and sometimes with a flashing light; combustible substances, such as sulphur, phosphorus, metallic sulphides, arsenic, sugar, gum, resin, &c., are inflamed by the peroxide of chlorine evolved. A finely-divided mixture of chlorate of potassium and excess of crystallised *oxalic acid* heated to about 70° C. gives off peroxide of chlorine mixed with carbonic anhydride, while chloride and acid oxalate of potassium remain (Calvert and Davies, Chem.

Soc. Qu. J. xi. 193). The reaction probably takes place in the manner represented by the equation:

$$3KClO^3 + 6C^2H^2O^4 = 2C^2KHO^4 + KCl + 2ClO^2 + 8CO^2 + 5H^2O.$$

Chlorate of potassium boiled with *strong nitric acid* yields nitrate and perchlorate of potassium, with evolution of chlorine and oxygen, but no peroxide of chlorine. (Penny, J. pr. Chem. xxiii. 296):

$$8KClO^3 + 6HNO^3 = 6KNO^3 + 2KClO^4 + Cl^6 + O^{13} + 3H^2O.$$

Dilute nitric acid free from nitrous acid does not act on chlorate of potassium, even when boiled; but if it contains *nitrous acid*, or if any reducing agent is present, such as tartaric acid, or arsenious acid, a lower oxide of chlorine is produced. If the temperature be kept below 5° C. the chief product is chlorous acid, $HClO^2$, the nitrous acid being at the same time reconverted into nitric acid: $HNO^2 + HClO^3 = HNO^3 + HClO^2$ (Millon, Ann. Ch. Pharm. xlvi. 298). Chlorate of potassium heated with hydrochloric acid, yields chloride of potassium, and gives off a mixture of peroxide of chlorine and free chlorine, called *euchlorine*, having the proportional composition of hypochlorous anhydride ($ClO^2 + Cl^3 = 2Cl^2O$). The reaction is:

$$4KClO^3 + 12HCl = 4KCl + 6H^2O + 3ClO^2 + Cl^9.$$

A mixture of chlorate of potassium and hydrochloric acid is much used as an oxidising agent, *e. g.* for the destruction of organic matter in toxicological investigations.

Chlorate of potassium heated with *pentachloride of phosphorus*, gives off a deep yellow gas which does not explode when heated, and when passed into dilute potash-ley, forms chloride, chlorate, and hypochlorite of potassium (H. Schiff, Ann. Ch. Pharm. cvi. 116).—Chlorate of potassium distilled with *iodine*, gives off a chloride of iodine, while chloride and iodate of potassium remain mixed with the excess of chlorate (Wöhler):

$$KClO^3 + I + I^x = KIO^3 + I^xCl.$$

Iodic acid added to solution of chlorate of potassium, forms crystals of neutral or acid iodate of potassium, while free chloric acid remains in solution. (Serullas.)

Chlorate of potassium is extensively used in the manufacture of lucifer matches and fire-works. Lucifer matches which take fire by friction, are tipped with a mixture of chlorate of potassium, phosphorus, and glue or gum.

Mixtures for producing fires of various colours, are composed as follows:

Red fire.		Green fire.		Purple fire.	
Nitrate of strontium	40 pts.	Nitrate of barium	77 pts.	Oxide of copper	12 pts.
Chlorate of potassium	6 „	Chlor. of potassium	8 „	Chlor. potassium	30 „
Fine charcoal	2 „	Fine charcoal	3 „		—
Sulphur	13 „	Sulphur	13 „	Sulphur	12 „

The following composition is applied to the interior of percussion caps, in quantities varying from 0·2 to 0·3 of a grain. Chlorate of potassium 26 pts., nitre 30, fulminate of mercury 12, sulphur 17, ground glass 14, gum 1 (= 100).

Chlorate of potassium is now extensively used as an oxidising agent in heightening the intensity of *steam-colours* on printed goods. It is of constant use in the laboratory as a source of oxygen, and is employed in medicine in the treatment of irritation of the mucous membranes. For the manufacture of gunpowder it is not well adapted, as the powder made with it, produces a very violent explosive force within a small space only, and bursts the gun instead of propelling the ball.

Chlorate of Silver, $AgClO^3$.—Obtained by dissolving oxide of silver in chloric acid, or by passing chlorine through water in which the oxide is suspended, filtering from chloride of silver, and evaporating. It crystallises in white opaque four-sided prisms, with oblique terminal faces (Vauquelin), of specific gravity 4·430 (Schröder); tastes like the nitrate. It deflagrates brightly on hot coals, and when mixed with sulphur, detonates violently on the slightest pressure. Hydrochloric, nitric, and acetic acid, convert it into chloride, with evolution of oxygen.

Chlorate of Sodium, $NaClO^3$.—This salt may be prepared by the action of chlorine on solution of soda; but it is difficult to separate from the chloride formed at the same time; the separation might, however, be effected by alcohol, which dissolves the chlorate much more easily than the chloride. The salt is likewise obtained by decomposing chlorate of potassium with silico-fluoride or acid tartrate of sodium, or chlorate of ammonium by carbonate of sodium (Wittstein). It might also be prepared by decomposing chlorate of calcium with carbonate of sodium.

Chlorate of sodium crystallises in regular tetrahedrons, modified by the faces of the opposite tetrahedron, also of the cube and rhomboïdal dodecahedron: the crystals are isomorphous with those of bromate of sodium. They dissolve in 3 times their weight of cold water, and in a smaller quantity of boiling water; also in 34 pts. of 83 per cent. alcohol at 16° C. and in a smaller quantity of hot alcohol.

CHLORATE OF STRONTIUM, $SrClO^3$.—Prepared like the barium-salt. Crystallises in deliquescent needles, or, according to Wächter, in large pyramidal crystals. It decomposes at the same temperature as the barium-salt, and deflagrates with purple flame on glowing coals.

CHLORATE OF URANIUM.—Protoxide of uranium dissolves in chloric acid, forming a green solution, which decomposes spontaneously, with evolution of chlorine and formation of uranic chloride. (Rammelsberg.)

CHLORATE OF ZINC, $ZnClO^3 + 3H^2O$, is obtained by dissolving carbonate of zinc or metallic zinc in chloric acid, chloride of zinc being also formed in the latter case; also by passing gaseous fluoride of silicon into water in which carbonate of zinc is suspended, and boiling the filtered liquid with chlorate of potassium. It crystallises, apparently, in octahedrons, has a very rough taste, and is soluble in water and alcohol.

CHLORETHERAL. Syn. with MONOCHLORETHYLIC ETHER. See ETHYL, OXIDE OF (ii. 643).

CHLORHYDRIC or **HYDROCHLORIC ACID.** HCl.—This gas is the only known compound of chlorine and hydrogen. Its solution in water has been used from very early times, and has received the names of *spirit of salt, muriatic acid, hydrochloric acid*, and *chlorhydric acid*. The gas was discovered by Priestley in 1772.

Natural Sources.—Hydrochloric acid gas is evolved from volcanos in eruption, and the acid solution is sometimes found in crevices on their slopes. It exists also, to the amount of 1 or 2 pts. in a thousand, in certain rivers of South America which have their source in volcanic formations.

Formation and Preparation.—1. Hydrochloric acid is produced by the direct union of chlorine and hydrogen. A mixture of the two gases in equal volumes, explodes violently if a burning body is introduced into it, or an electric spark passed through it, or if it be exposed to direct sunshine (Gm. ii. 319). No combination takes place in the dark, but if the mixture be exposed to diffused daylight, the gases combine gradually. Thus, if two bottles of exactly equal capacity and fitted to one another by grinding, are filled by displacement with chlorine and hydrogen respectively, then adapted to each other by their mouths, the chlorine-vessel being placed uppermost, and set aside for some hours in a light situation, but not in direct sunshine, the green colour of the chlorine will gradually disappear almost entirely, and a few minutes' exposure to sunshine will complete the combination. If the two bottles be then separated under mercury, each will be found full of hydrochloric acid gas, no gas escaping and no rising of the mercury taking place in either bottle, showing that the chlorine and hydrogen have combined without expansion or contraction. If a jet of water tinged with blue litmus be thrown up into either of the bottles, the gas will be rapidly and completely absorbed, while the litmus solution will assume a bright red colour. Any bleaching of the litmus would indicate free chlorine; any unabsorbed gas, the presence of free hydrogen; in this manner, an excess of either gas in the original mixture may be detected.

2. Hydrochloric acid gas is usually prepared by the action of sulphuric acid on fused chloride of sodium. There is at first a copious effervescence, which, after some time, it may be necessary to revive by the application of a gentle heat. The reaction is:

$$NaCl + H^2SO^4 = NaHSO^4 + HCl.$$

The gas must be collected over the mercurial trough, as it is rapidly absorbed by water.

3. Hydrochloric acid may also be produced by the action of water on certain chlorides. The two chlorides of phosphorus are decomposed immediately and completely by mixture with an excess of water, with formation of phosphorous and phosphoric acid respectively, thus:

$$PCl^3 + 3H^2O = H^3PO^3 + 3HCl.$$
$$PCl^5 + 4H^2O = H^3PO^4 + 5HCl.$$

The two chlorides of antimony are decomposed more slowly. Trichloride of bismuth requires prolonged treatment with water to effect its thorough decomposition, which, however, takes place readily at a boiling temperature. Stannic chloride, even at a boiling temperature, is decomposed very imperfectly. The sesquichloride of aluminium and protochloride of magnesium, &c., are decomposed by steam, with evolution of hydrochloric acid, at temperatures considerably below redness:

$$2Al^2Cl^3 + 3H^2O = Al^4O^3 + 6HCl.$$
$$2MgCl + H^2O = Mg^2O + 2HCl.$$

Moreover, hydrochloric acid results from the reaction of chloride of phosphorus, chloride of antimony, and some other chlorides, usually hyperchlorides, not only with water, but with most oxyhydrogenised compounds (pp. 897—900).

4. Hydrochloric acid is a constant attendant upon the direct action of chlorine on hydrogenised substances. A solution of chlorine in water is converted, when exposed to light, into hydrochloric and hypochlorous acids: $Cl^2 + H^2O = HCl + HClO$. Chlorine instantly decomposes sulphydric acid, with formation of hydrochloric acid and separation of sulphur: $Cl^2 + H^2S = 2HCl + S$. Phosphoretted and arsenetted hydrogen are likewise decomposed by chlorine, with formation of hydrochloric acid. Numerous organic compounds also are decomposed by chlorine, one portion of that element uniting with the whole or with part of the hydrogen, and an equal portion taking the place of the hydrogen thus removed: *e. g.*

$$\underset{\text{Acetic acid.}}{C^2H^4O^2} + 3Cl^2 = \underset{\text{Trichlor-acetic acid.}}{C^2HCl^3O^2} + 3HCl.$$

Hydrochloric acid also results from the inverse action of hydrogen upon a chlorine compound, as when ignited chloride of nickel is subjected to a current of hydrogen, thus: $NiCl + H = HCl + Ni$.

Properties.—Hydrochloric acid is a colourless gas, having a strong acid taste, and a pungent irritating odour. Its specific gravity (air = 1) is, according to the determination of Biot and Gay-Lussac, 1·27; by calculation, it is $\frac{35\cdot5 + 1}{2} \times 0\cdot0693 = 1\cdot265$. It forms opaque white fumes in the air, owing to its union with, and condensation of, the atmospheric moisture. In perfectly dry air these fumes are not produced. The gas is extremely soluble in water. When a flask of dry hydrochloric acid is opened under water, the whole of the gas is absorbed in an instant, and the flask not unfrequently broken by the violent rush of liquid. At mean temperature (15° C.) water dissolves about 458 times its volume of the gas (see GASES, ABSORPTION OF). At the temperature of 10°, under a pressure of 40 atmospheres, hydrochloric acid is condensed into a colourless liquid, having a specific gravity 1·27. It has never been solidified. Hydrochloric acid is not inflammable, and extinguishes most burning bodies, but when a piece of potassium is introduced by means of an iron wire into a tube full of the gas retained over mercury, and is then heated to redness by a spirit-lamp applied externally, it undergoes combustion, unites with the chlorine, and leaves the hydrogen, which is eventually found to occupy exactly one half the volume of the original gas: $HCl + K = KCl + H$.

Solution of hydrochloric acid is usually made from common salt and sulphuric acid diluted with about two-thirds its bulk of water. The reaction is effected in a retort to which a gentle heat is applied, and the evolved gas is condensed in a vessel or series of vessels of distilled water. The condensing liquid increases considerably in bulk, and may eventually be made to acquire a specific gravity of 1·21, under which circumstances it consists of one atom of hydrochloric acid, HCl, dissolved in three atoms of water, H^2O. Solution of hydrochloric acid has usually a specific gravity of 1·162, and then consists of one atom of hydrochloric acid HCl, dissolved in four atoms of water, H^2O.

Commercial muriatic acid is made by heating in iron cylinders two proportions of common salt, with as much brown sulphuric acid as contains one proportion of real acid, and condensing the evolved gas in water contained in a series of stoneware Woulfe's bottles. The reaction is: $H^2SO^4 + 2NaCl = Na^2SO^4 + 2HCl$. For details, see *Ure's Dictionary of Arts, Manufactures and Mines*, ii. 481.—Pelouze et Frémy, *Traité de Chimie générale*, 3^{me} éd. i. 436.—Payen, *Précis de Chimie industrielle*, 4^{me} éd. i. 264.)

The commercial acid, which frequently contains, as impurities, sulphurous acid, arsenious acid, sesquichloride of iron, stannic chloride, and even free chlorine, may be partly purified by dilution and redistillation. A pure solution of hydrochloric acid is usually colourless, but when in large quantities, has a very pale yellowish green tint. The slight yellow colour of miscalled pure acid is generally due to the presence of free chlorine, but the bright deep yellow of the commercial acid results from the presence of chloride of iron. The introduction of a small quantity of organic matter, as by contact with a cork, will likewise impart a yellow colour to hydrochloric acid otherwise pure.

A strong solution of hydrochloric acid evolves fumes on exposure to air. When boiled, it gives off hydrochloric acid gas, until the temperature slightly exceeds 100° C., when there distils over a diluted solution of the acid, having a specific gravity of 1·1, and consisting of 1 atom of hydrochloric acid, HCl, dissolved in 8 atoms of water, H^2O.

From the experiments of **Roscoe**, however (Chem. Soc. Qu. J. xiii. 156), it appears that the composition of aqueous hydrochloric acid (and of other aqueous acids), of constant boiling point, varies with the pressure, and that there exists for each pressure a corresponding aqueous acid, which undergoes no change in composition when distilled under this pressure, and therefore has a constant boiling point. In table A, column P shows the pressure in metres of mercury under which aqueous hydrochloric acid must be distilled to attain the composition given in the next column.

TABLE A.—*Percentage of* HCl *in aqueous Hydrochloric Acid boiling under different Pressures.*

P	Percentage of HCl.	P	Percentage of HCl.	P	Percentage of HCl.	P	Percentage of HCl.
0·05	23·2	0·7	20·4	1·3	19·3	2·0	18·5
0·1	22·9	0·76	20·14	1·4	19·1	2·1	18·4
0·2	22·3	0·8	20·2	1·5	19·0	2·3	18·3
0·3	21·8	0·9	19·9	1·6	18·9	2·4	18·1
0·4	21·4	1·0	19·7	1·7	18·8	2·5	18·0
0·5	21·1	1·1	19·5	1·8	18·7		
0·6	20·7	1·2	19·4	1·9	18·6		

The acid which boils constantly under the pressure 0·76 met., and contains 20·24 per cent. HCl, is the hydrate above mentioned, $HCl.8H^{2}O$. The table shows that the percentage of HCl in the aqueous acid of constant boiling point, diminishes with increase of pressure.

When aqueous hydrochloric acid is vaporised by passing a current of dry air through it at a *given temperature*, a point is likewise reached beyond which no decomposition occurs. In Table B the first column gives the temperatures, the second the percentage of HCl contained in the acid, unalterable at the corresponding temperature.

TABLE B.—*Percentage of* HCl *in Aqueous Hydrochloric Acid of constant composition at different Temperatures.*

T°	Percentage of HCl.	T°	Percentage of HCl.	T°	Percentage of HCl.	T°	Percentage of HCl.
0° C.	25·0	30° C.	24·1	60° C.	23·0	90° C.	21·4
5	24·9	35	23·9	65	22·8	95	21·1
10	24·7	40	23·8	70	22·6	100	20·7
15	24·6	45	23·6	75	22·3		
20	24·4	50	23·4	80	22·0		
25	24·3	55	23·2	85	21·7		

The specific gravity of aqueous hydrochloric acid, of various degrees of concentration has been determined by Ure and by E. Davy. The results are given in Tables C and D; it will be observed that the specific gravities as determined by Davy are rather lower for each percentage of HCl than those of Ure.

TABLE C.—*Percentage of* HCl *in Aqueous Hydrochloric Acid at* 25° C. (77° F.) *according to* E. Davy.

Sp. Gr.	HCl.	Sp. Gr.	HCl.	Sp. Gr.	HCl.	Sp. Gr.	HCl.
1·21	42·43	1·16	32·32	1·11	22·22	1·06	12·12
1·20	40·80	1·15	30·30	1·10	20·20	1·05	10·10
1·19	38·38	1·14	28·28	1·09	18·18	1·04	8·08
1·18	36·36	1·13	26·26	1·08	16·16	1·03	6·06
1·17	34·34	1·12	24·24	1·07	14·14	1·02	4·04
						1·01	2·02

Table D.—*Composition of Aqueous Hydrochloric Acid according to* Ure.

Acid of Sp. gr. 1·2.	Specific Gravity.	Chlorine. per cent	HCl. per cent.	Acid of sp. gr. 1·2.	Specific Gravity.	Chlorine. per cent.	HCl. per cent.	Acid of sp. gr. 1·2.	Specific Gravity.	Chlorine. per cent	HCl. per cent.
100	1·2000	39·675	40·777	66	1·1328	26·186	26·913	32	1·0637	12·697	13·049
99	1·1982	39·278	40·369	65	1·1308	25·789	26·505	31	1·0617	12·300	12·641
98	1·1964	38·882	39·961	64	1·1287	25·392	26·098	30	1·0597	11·903	12·233
97	1·1946	38·485	39·554	63	1·1267	24·996	25·690	29	1·0577	11·506	11·825
96	1·1928	38·089	39·146	62	1·1247	24·599	25·282	28	1·0557	11·109	11·418
95	1·1910	37·692	38·738	61	1·1226	24·202	24·874	27	1·0537	10·712	11·010
94	1·1893	37·296	38·330	60	1·1206	23·805	24·466	26	1·0517	10·316	10·602
93	1·1875	36·900	37·923	59	1·1185	23·408	24·058	25	1·0497	9·919	10·194
92	1·1857	36·503	37·516	58	1·1164	23·012	23·050	24	1·0477	9·522	9·786
91	1·1846	36·107	37·108	57	1·1143	22·615	23·242	23	1·0457	9·125	9·379
90	1·1822	35·707	36·700	56	1·1123	22·218	22·834	22	1·0437	8·729	9·971
89	1·1802	35·310	36·292	55	1·1102	21·822	22·426	21	1·0417	8·332	8·563
88	1·1782	34·913	35·884	54	1·1082	21·425	22·019	20	1·0397	7·935	8·155
87	1·1762	34·517	35·476	53	1·1061	21·028	21·611	19	1·0377	7·538	7·747
86	1·1741	34·121	35·068	52	1·1041	20·632	21·203	18	1·0357	7·141	7·340
85	1·1721	33·724	34·660	51	1·1020	20·235	20·796	17	1·0337	6·745	7·932
84	1·1701	33·328	34·252	50	1·1000	19·837	20·388	16	1·0318	6·348	6·524
83	1·1681	32·931	33·845	49	1·0980	19·440	19·980	15	1·0298	5·951	6·116
82	1·1661	32·535	33·437	48	1·0960	19·044	19·572	14	1·0279	5·554	6·709
81	1·1641	32·136	33·029	47	1·0939	18·647	19·165	13	1·0259	5·158	5·301
80	1·1620	31·746	32·621	46	1·0919	18·250	18·757	12	1·0239	4·762	5·893
79	1·1599	31·343	32·213	45	1·0899	17·854	18·359	11	1·0220	4·365	4·486
78	1·1578	30·946	31·805	44	1·0879	17·457	17·941	10	1·0200	3·968	4·078
77	1·1557	30·550	31·398	43	1·0859	17·060	17·534	9	1·0180	3·571	4·670
76	1·1536	30·153	30·990	42	1·0838	16·664	17·126	8	1·0160	3·174	3·262
75	1·1515	29·757	30·582	41	1·0818	16·267	16·718	7	1·0140	2·778	3·854
74	1·1494	29·361	30·174	40	1·0798	15·870	16·310	6	1·0120	2·381	3·447
73	1·1473	28·964	29·767	39	1·0778	15·474	15·902	5	1·0100	1·984	2·039
72	1·1452	28·567	29·359	38	1·0758	15·077	15·494	4	1·0080	1·588	2·631
71	1·1431	28·171	28·951	37	1·0738	14·680	15·087	3	1·0060	1·191	1·224
70	1·1410	27·772	28·544	36	1·0718	14·284	14·679	2	1·0040	0·795	1·816
69	1·1389	27·376	28·136	35	1·0697	13·887	14·271	1	1·0020	0·397	1·408
68	1·1369	26·979	27·728	34	1·0677	13·490	13·863				
67	1·1349	26·583	27·321	33	1·0657	13·094	13·456				

Aqueous hydrochloric acid possesses powerful acid properties, reddens litmus, tastes intensely sour, effervesces with carbonates, and dissolves many metals with evolution of hydrogen. It does not bleach vegetable colours or dissolve gold leaf. W. O.

CHLORHYDRIC ETHERS. See Chlorides of Alcohol-Radicles (p. 897).

CHLORHYDRINS. (Berthelot, Ann. Ch. Phys. [3] xli. 296.—Berthelot and De Luca, *ibid.* xlviii. 304; lii. 433.)—These compounds, which are precisely analogous to the bromhydrins (p. 667), are the chlorhydric ethers of glycerin, and may be regarded as derived therefrom by the substitution of one or more atoms of chlorine for an equivalent quantity of peroxide of hydrogen. They are produced, either by the action of hydrochloric acid or of the chlorides of phosphorus on glycerin; the latter method does not however yield very good products.

Monochlorhydrin, $C^3H^7ClO^2 = (C^3H^5)'''.(HO)^2.Cl$, is obtained by saturating gently heated glycerin with hydrochloric acid gas; then keeping the liquid at 100° C. for some hours; saturating with carbonate of sodium; agitating with ether; distilling the residue left after evaporation of the ether; and again treating it with carbonate of sodium and ether. It is a neutral oil, having a fresh ethereal odour and a sweet taste, with pungent after-taste. Specific gravity 1·31. It remains perfectly fluid at −35° C.; boils at 227°; burns with a white, green-edged flame, emitting hydrochloric acid. Oxide of lead saponifies it slowly. It does not immediately precipitate nitrate of silver. It mixes with its own bulk of water. With 8 or 10 times its bulk of water, it forms a very stable emulsion. It also mixes with ether.

Dichlorhydrin, $C^3H^6Cl^2O = (C^3H^5)'''.HO.Cl^2$, is obtained by heating a solution of glycerin in 10 or 12 times its weight of fuming hydrochloric acid, to 100° C. for three or four days, purifying the product with carbonate of sodium and ether as above, and evaporating, first over the water-bath, then in vacuo. It is a neutral oil, having an ethereal odour. Specific gravity 1·37. It boils at 178° C.; remains quite fluid at −35°; burns like the preceding; is easily decomposed by potash, yielding chloride of potassium and glycerin; mixes with ether, but does not form a stable emulsion with water.

Trichlorhydrin; Trichloride of Glyceryl, $C^3H^5Cl^3$.—Produced by the action of pentachloride of phosphorus on dichlorhydrin:

$$C^3H^4Cl^2O + PCl^5 = PCl^3O + HCl + C^3H^5Cl^3.$$

It is a neutral liquid, much more stable than tribromhydrin. Volatilises at about 155° C. (Berthelot and De Luca.)

Epichlorhydrin. Oxychloride of Glyceryl. C^3H^5ClO.—Obtained by treating dichlorhydrin with hydrochloric acid gas, or with the fuming acid. Neutral oil, resembling dichlorhydrin. Distils between 120° and 130° C. (Berthelot.)

Epidichlorhydrin. Dichloride of Glycerylene. $C^3H^4Cl^2$. — Produced in small quantity in the preparation of trichlorhydrin and bromodichlorhydrin, probably by a secondary reaction, inasmuch as it differs from dichlorhydrin by H^2O, and from trichlorhydrin by HCl. It is isolated and purified by repeated fractional distillation. Neutral liquid, volatile at about 120° C. Treated with moist oxide of silver, it slowly reproduces glycerin. (Berthelot and De Luca.)

Dibromochlorhydrin, $C^3H^5Br^2Cl$.—Produced by the action of pentachloride of phosphorus on dibromhydrin. Neutral liquid, volatile at about 200° C. With moist oxide of silver at 100°, it slowly reproduces glycerin. It is isomeric with dibromide of chlorotritylene, $C^3H^5ClBr^2$.

Bromodichlorhydrin, $C^3H^5BrCl^2$.—Produced by the action of pentabromide of phosphorus on dichlorhydrin. Neutral liquid, volatile at about 176° C. Isomeric with dichloride of bromotritylene.

With moist oxide of silver at 100°, it slowly reproduces glycerin; at the same time, however, a small quantity of carbonic anhydride is formed by oxidation, together with crystalline scales, which appear to be propionate of silver:

$$C^3H^5BrCl^2 + 3H^2O = \underset{\text{Glycerin.}}{C^3H^8O^3} + 2HCl + HBr$$

and

$$C^3H^5BrCl^2 + 2H^2O = \underset{\text{Propionic acid.}}{C^3H^6O^2} + 2HCl + HBr$$

For the Acetochlorhydrins, see p. 25; Benzochlorhydrins (p. 547.)

CHLORHYDROPHENIDE. Chloride of Phenyl. (See Phenyl.)

CHLORHYDROPROTEIC ACID. A name applied by Mulder (J. pr. Chem. xvii. 316), to the precipitate formed by hydrochloric acid in a solution of albumin, said by Mulder to contain 3·7 per cent. of hydrochloric acid. It is probably however nothing but albumin.

CHLORIDES. The term chloride is applied to all compounds of chlorine which may be derived from one or more atoms of hydrochloric acid, H^nCl^n, by the substitution of a metal or other radicle (which may itself contain chlorine), for an equivalent quantity of hydrogen. Those which are volatile contain, in two volumes of vapour, 1, 2, 3, &c. atoms of chlorine, according as the radicle with which the chlorine is associated is mono-, di-, tri-atomic, &c.*, thus:

2 vol.	chloride of	ethyl,	$C^2H^5.Cl$,	contain	1	at. chlorine
„	„	sulphuryl,	$(SO^2)''.Cl^2$	„	2	„
„	„	boron,	$\overset{'''}{B}.Cl^3$	„	3	„
„	„	silicium,	$\overset{''''}{Si}Cl^4$	„	4	„

Chlorides may be conveniently divided into the following groups, each of which contains compounds derived from one or more atoms of hydrochloric acid.

a. **Metallic Chlorides.** Chlorine combines with all metals, the number of chlorine-atoms in the resulting molecule varying from 1 to 7.

a. Chlorides, with one atom of chlorine, formed on the type of the single atom of hydrochloric acid, HCl, namely, protochlorides, MCl, and hemichlorides, or subchlorides, M^2Cl. The greater number of metals form protochlorides, all indeed, except aluminium, antimony, arsenic, bismuth, tantalum, titanium, tungsten, vanadium and zirconium. The protochlorides are all more or less soluble in water, except those of silver and platinum, which are quite insoluble. The protochlorides of gold, platinum,

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* If, however, the radicle contains chlorine, this statement must be understood as applying only to the portion of chlorine which is not thus included, and is removable by water or by aqueous potash; for example, 2 vols. chloride of trichloracetyl, $C^2Cl^3O.Cl$ contain 4 atoms of chlorine; but only one of these is removable by water, the compound, treated with water, yielding hydrochloric acid and trichloracetic acid ($C^2Cl^3O.Cl + H^2O = HCl + C^2Cl^3O.H.O$).

and palladium, are completely decomposed at a red heat; that of copper, partially. The other protochlorides melt when heated, and volatilise unchanged at higher temperatures. Several hydrated protochlorides, those of magnesium and zinc, for instance, are resolved more or less completely by heat into metallic oxide and hydrochloric acid. The fused protochlorides are electrolytic.

The *hemi-atomic metals*, especially copper and mercury, form subchlorides, containing, *e. g.* Cu^2Cl, Hg^2Cl. They are insoluble in water, and under certain circumstances manifest a tendency to break up into metal and protochloride.

β. *Chlorides with two atoms of chlorine, formed on the type* H^2Cl^2, *namely*, Dichlorides, $M''Cl^2$. The metals which form dichlorides, are molybdenum, palladium, platinum, tellurium, tin, titanium, tungsten, and vanadium. The dichlorides of platinum and palladium give off at a gentle heat one half, and at a stronger heat the whole of their chlorine. The others are easily volatile.

γ. *Chlorides with three atoms of chlorine, formed on the type* H^3Cl^3, namely, Trichlorides, $M'''Cl^3$, and sesquichlorides, $(M^2)'''Cl^3$.—The metals which form trichlorides are antimony, arsenic, bismuth, gold, molybdenum, tungsten, and vanadium. Trichloride of gold is reduced at a gentle heat to protochloride, which at a higher temperature is resolved into chlorine and metal. The rest volatilise unchanged. The trichlorides of antimony and bismuth are very fusible solids; the rest are liquids. The volatile trichlorides are decomposed by water, yielding hydrochloric acid and an oxychloride, thus: $BiCl^3 + H^2O = 2HCl + BiClO$.

The sesquichlorides are formed from a triple molecule of hydrochloric acid, by the substitution of 2 at. of a sesqui-atomic metal for 3 at. hydrogen; the metals which form them are aluminium, cerium (?), chromium, iron, and manganese. The cerium and manganese compounds are known only as hydrates; the rest are fusible and volatile solids. They are all soluble in water, and are partially decomposed by heat.

δ. *Chlorides with four atoms of chlorine, formed on the type* H^4Cl^4, *namely*, Tetrachlorides. These are formed only by the metals tin, titanium, and zirconium. The first two are liquids, the third solid: they are all volatile, and their general behaviour shows that two of the chlorine-atoms are retained less forcibly than the other two. The tetrachlorides of tin and titanium are soluble in water; the zirconium-compound is decomposed by water.

ε. *Chloride with 5 at. chlorine.*—Pentachloride of antimony, $SbCl^5$. Volatile liquid, decomposed by water.

There are no *hexachlorides* known, and only one *heptachloride*, namely, the heptachloride of manganese, Mn^2Cl^7.

Formation of Metallic Chlorides.—Chlorides are generally prepared by one or other of the following processes. α. By acting upon the metal with chlorine gas. This method is frequently employed for the preparation of anhydrous chlorides. The pentachloride of antimony and protochloride of copper are examples of chlorides sometimes produced in this manner. The chlorides of gold and platinum are usually prepared by acting upon the metals with nascent chlorine, developed by the mutual action of hydrochloric and nitric acids. Sometimes, on the other hand, the metal is in a nascent state, as when titanic chloride is formed by passing a current of chlorine over a heated mixture of charcoal and titanic anhydride. The chlorides of aluminium and chromium may be obtained by similar processes.

β. Chlorine gas, by its action upon metallic oxides, drives out the oxygen, and unites with the respective metals to form chlorides. This reaction sometimes takes place at ordinary temperatures, as is the case with oxide of silver; sometimes only at a red heat, as is the case with the oxides of the alkali- and alkaline earth-metals. The hydrates and carbonates of these last metals, when dissolved or suspended in hot water and treated with excess of chlorine, are converted, chiefly into chlorides, partly into chlorates.

γ. Many metallic chlorides are prepared by acting upon the metals with hydrochloric acid. Zinc, cadmium, iron, nickel, cobalt, and tin dissolve readily in hydrochloric acid, with liberation of hydrogen; copper only in the strong boiling acid; silver, mercury, palladium, platinum, and gold, not at all. Sometimes the metal is substituted, not for hydrogen, but for some other metal. Stannous chloride, for instance, is frequently made by distilling metallic tin with mercuric chloride, thus: $2HgCl + Sn = SnCl^2 + Hg^2$.

δ. Or the oxide, hydrate, or carbonate of metal may be dissolved in hydrochloric acid. In this way the hydrated protochloride of copper and sesquichloride of iron are usually made:

$$Cu^2O + 2HCl = H^2O + 2CuCl.$$
$$Fe^2H^3O^3 + 3HCl = 3H^2O + Fe^2Cl^3.$$

With a peroxide, the reaction is accompanied by an evolution of chlorine, thus:

$$Pb^2O^2 + 4HCl = 2H^2O + 2PbCl + Cl^2.$$

ε. Chloride of silver and mercurous chloride, which are insoluble in water, and chloride of lead, which is but sparingly soluble, are easily formed by precipitating any of the corresponding soluble salts with a soluble chloride, thus:

$$NaCl + AgNO^3 = AgCl + NaNO^3.$$

Decompositions.—1. The action of heat upon chlorides has been already noticed. Most protochlorides volatilise at high temperatures, without decomposition; the higher chlorides give off part of their chlorine when heated.—2. Some chlorides which resist the action of heat alone are decomposed by ignition in the air, yielding metallic oxides and free chlorine: this is the case with the chlorides of iron and manganese; but most protochlorides remain undecomposed, even in this case.—3. All metallic chlorides, excepting those of the alkali-metals and earth-metals, are decomposed at a red heat by *hydrogen* gas, with formation of hydrochloric acid: in this way, metallic iron may be obtained in fine cubical crystals. Chloride of silver placed in contact with metallic zinc or iron, under dilute sulphuric or hydrochloric acid, is reduced to the metallic state by the *nascent hydrogen.*—4. Metallic chlorides, which are not decomposed by heat alone, likewise resist the action of *charcoal* at a white heat, but if *aqueous vapour* is likewise present, decomposition takes place, the metal being reduced, and hydrochloric acid formed, together with an oxide of carbon, *e.g.*:

$$2AgCl + H^2O + C = Ag^2 + 2HCl + CO.$$

—5. Metallic chlorides are not decomposed by heating with *sulphur*, but *phosphorus* decomposes several of them.—6. Those metallic chlorides which are not decomposed by heat alone, likewise resist decomposition when heated to whiteness with *boric anhydride*, or *silicic anhydride*; but if water is present, hydrochloric acid is evolved, and a borate or silicate of the metal is produced. Vapour of *sulphuric anhydride*, however, decomposes certain metallic chlorides, a sulphate being formed, and a mixture of equal volumes of chlorine and sulphurous anhydride evolved, *e.g.*:

$$2NaCl + 2SO^3 = Na^2SO^4 + SO^2 + Cl^2.$$

—7. *Sulphuric, phosphoric, boric*, and *arsenic acids*, decompose most metallic chlorides, sometimes at ordinary, sometimes at higher temperatures.—8. All metallic chlorides heated with *peroxide of lead* or *manganese* and *sulphuric acid*, give off chlorine, *e.g.*:

$$2NaCl + Mn^2O^2 + 2H^2SO^4 = Na^2SO^4 + Mn^2SO^4 + 2H^2O + Cl^2.$$

—9. Distilled with *sulphuric acid* and *chromate of potassium*, they yield a dark bluish-red distillate of chloro-chromic acid.—10. Some metallic chlorides are decomposed by *water*, forming hydrochloric acid and an oxychloride, *e.g.*: $BiCl^3 + H^2O = 2HCl + BiClO$. The chlorides of antimony and stannous chloride are decomposed in a similar manner.—11. All soluble chlorides give with solution of *nitrate of silver*, a white precipitate of chloride of silver, easily soluble in ammonia, insoluble in nitric acid. With *mercurous nitrate*, they yield a white curdy precipitate of mercurous chloride, blackened by ammonia; and with *lead-salts*, not too dilute, a white crystalline precipitate of chloride of lead, soluble in excess of water.

Combinations.—Metallic chlorides unite with each other and with the chlorides of the non-metallic elements, forming such compounds as chloromercurate of potassium, $KCl.HgCl$, chloroplatinate of sodium, $NaCl.PtCl^2$, chloriodate of potassium, $KCl.ICl^3$, &c. They also combine with oxides and sulphides, forming oxychlorides and sulphochlorides. Metallic chlorides likewise combine in definite proportions with ammonia and organic bases; the chlorides of platinum form with ammonia the compounds $NH^3.PtCl$, $2NH^3.PtCl$, $NH^3.PtCl^2$, and $2NH^3.PtCl^2$; mercuric chloride forms with phenylamine the compound $C^6H^7N.HgCl$; with chinoline, $C^9H^7N.2HgCl$, &c. Many of these compounds may be regarded as chlorides of metalloïdal radicles, formed on the ammonium type: thus, ammonio-protochloride of platinum, $NH^3.PtCl$ = chloride of platammonium $(NH^3Pt).Cl$.

Many metallic chlorides are soluble in alcohol, ether, volatile oils, &c.

b. **Chlorides of Organo-metallic Radicles** (including Phosphorus-bases).—These compounds, which bear considerable resemblance to the simple metallic chlorides, are produced, either by the direct union of chlorine with the organo-metallic radicle, or by the action of hydrochloric acid on the oxide or hydrate of that radicle. Some of them are volatile liquids; others crystalline solids. They contain 1, 2, 3, or 4 at. of chlorine associated with 1 molecule of the organo-metallic radicle, those which contain an even number of atoms of alcohol-radicle forming mono- and trichlorides, while those which contain an uneven number of atoms of alcohol-radicle form di- and tetrachlorides, thus:

Arsen-monomethyl	forms	$AsMeCl^3$	and	$AsMeCl^4$
Arsen-dimethyl	,,	$AsMe^2Cl$	,,	$AsMe^2Cl^3$
Stib-triethyl	,,	$SbMe^3Cl^2$		
Stib-tetramethylium	,,	$SbMe^4Cl$		

All these compounds may be regarded as derived from a molecule of tri- or pentachloride of arsenic or antimony by the substitution of an alcohol-radicle for an equivalent quantity of chlorine (pp. 339, 397, 411).

3. **Chlorides of Alcohol-Radicles.** *Hydrochloric or Chlorhydric Ethers.*—These compounds may be regarded as derived from hydrochloric acid in a similar manner to the metallic chlorides, or from the corresponding alcohols by the substitution of chlorine for an equivalent quantity of peroxide of hydrogen, *e. g.*:

Chloride of ethyl,	$C^2H^5.Cl$	from	Ethylic alcohol,	$C^2H^5.HO$
Chloride of ethylene,	$C^2H^4.Cl^2$	,,	Glycol,	$C^2H^4.(HO)^2$
Chloride of glyceryl,	$C^3H^5.Cl^3$	,,	Glycerin,	$C^3H^5.(HO)^3$

a. The *monatomic alcoholic chlorides* are obtained:

1. By the action of hydrochloric acid on the alcohols:

$$C^2H^5.H.O + HCl = H^2O + C^2H^5.Cl.$$

2. By the action of the chlorides of phosphorus, or of oxychloride of phosphorus, on the alcohols:

$$3(C^2H^5.H.O) + PCl^3 = H^3PO^3 + 3C^2H^5Cl.$$
$$3(C^2H^5.H.O) + PCl^3O = H^3PO^4 + 3C^2H^5Cl.$$

3. By the action of chlorine on the corresponding hydrides. This reaction has been observed only in the case of hydride of benzyl (p. 573).

Most of these monatomic chlorides are liquids more volatile than the corresponding alcohols: one, viz. chloride of methyl, is gaseous at ordinary temperatures, and chloride of cetyl is solid. Treated with alcoholic potash, they yield chloride of potassium and an alcohol:

$$C^2H^5Cl + KHO = KCl + C^2H^5.H.O$$

When recently prepared, they do not precipitate nitrate of silver immediately; but when they are heated with it in sealed tubes, a slow precipitation takes place. Sodium at ordinary temperatures decomposes them, with formation of chloride of sodium and an alcohol-radicle:

$$\underset{\text{Chloride of octyl.}}{2C^8H^{17}Cl} + Na^2 = 2NaCl + \underset{\text{Octyl.}}{C^8H^{17}.C^8H^{17}}.$$

But if heat be applied, the sodium assumes a violet tint and swells up considerably. The liquid then becomes hot; hydrogen is evolved; the violet colour disappears; and a pasty mass is ultimately obtained, consisting of chloride of sodium and an oil, which is the corresponding hydrocarbon, C^nH^{2n}: thus, with chloride of octyl:

$$2(C^8H^{17}.Cl) + Na^2 = 2(C^8H^{16}Na.Cl) + HH$$

and:

$$\underset{\text{Violet substance.}}{C^8H^{17}Na.Cl} = NaCl + \underset{\text{Octylene.}}{C^8H^{16}}.$$

The same violet substance is produced by the simultaneous action of chlorine and sodium on octylene. It quickly turns white in contact with the air, yielding soda and chloride of sodium, and is quickly decomposed by water, alcohol, and other liquids containing oxygen (Bouis, N. Ann. Chim. Phys. xliv. 114). A similar violet substance is formed by the action of potassium on chloride of phenyl.

β. The *diatomic alcoholic chlorides* are produced: 1. By the direct union of chlorine with the corresponding diatomic hydrocarbons, *e. g.* chloride of ethylene, chloride of tetrylene, &c.—2. By the action of pentachloride of phosphorus on the corresponding alcohols, *e. g.*:

$$\underset{\text{Glycol.}}{C^2H^4.H^2.O^2} + 2PCl^5 = \underset{\text{Chloride of ethylene.}}{C^2H^4Cl^2} + 2POCl^3 + 2HCl.$$

Two series of these chlorides are known, containing the radicles C^nH^{2n}, homologous with ethylene, and C^nH^{2n-8}, homologous with benzylene.

The chlorides $C^nH^{2n}Cl^2$, are liquids, for the most part volatile without decomposition. They are decomposed by chlorine, yielding substitution-products. Heated with alcoholic potash, they yield chloride of potassium, and the chloride of an aldehyde-radicle:

$$C^2H^4Cl^2 + KHO = C^2H^3Cl + KCl + H^2O.$$

Sulphide of potassium simply converts them into sulphides of diatomic alcohol-radicles:

$$C^2H^4Cl^2 + K^2S = 2KCl + C^2H^4S.$$

Heated with ammonia in sealed tubes, they appear to yield the same products as the corresponding bromides, viz. diamines containing 1, 2, or 3 at. of the radicles C^nH^{2n}; but the reactions have not been so much examined as those of the bromides. (See AMMONIUM-BASES, p. 196; also ETHYLENE-BASES.)

The chlorides $C^nH^{2n-8}Cl^2$, are also volatile liquids heavier than water. Heated with alcoholic potash, they yield chloride of potassium and an aldehyde: *e. g.* chloride of benzylene yields bitter-almond oil. (Wicke, Ann. Ch. Pharm. cii. 356):

$$C^7H^6Cl^2 + KHO = KCl + HCl + C^7H^6O.$$

Ammonia heated with chloride of benzylene in sealed tubes, acts in like manner (Wicke). With alcoholic sulphide of potassium, they are decomposed like the chlorides last mentioned, yielding diatomic sulphides.

γ. Of *triatomic alcoholic chlorides*, only one is known, viz. chloride of glyceryl or trichlorhydrin, $(C^3H^5)'''Cl^3$, which is produced by the action of pentachloride of phosphorus on dichlorhydrin, $(C^3H^5)'''\begin{matrix}HO\\Cl^2\end{matrix}$. (See CHLORHYDRINS, p. 894.)

4. **Chlorides of Aldehyde-Radicles.**—These are monatomic chlorides of the general form $C^nH^{2n-1}Cl$, isomeric with the monochlorinated diatomic alcohol-radicles, *e. g. chloride of vinyl*, $C^2H^3.Cl$, with chlorethylene, $C^2(H^3Cl)$. They are obtained by the action of alcoholic potash on the chlorides of the diatomic alcohol-radicles (p. 987), sometimes also by that of oxychloride of carbon on the aldehydes, *e. g.* C^2H^3Cl from acetic aldehyde, C^2H^4O (Harnitzky, p. 107). It is probable also that they might be obtained by treating the aldehydes with pentachloride of phosphorus; as butyral, the isomer of butylic aldehyde, yields when thus treated, the compound C^4H^7Cl (p. 689).

These chlorides are volatile liquids, except chloride of vinyl, which is gaseous at ordinary temperatures. Chlorine converts them into dichlorides of chlorinated alcohol-radicles.

5. **Chlorides of Acid Radicles.**—These compounds may be derived from acids by the substitution of chlorine for peroxide of hydrogen, *e. g.*:

Chloride of acetyl,	$C^2H^3O.Cl$	from	Acetic acid,	$C^2H^3O.HO$
Chloride of sulphuryl,	$(SO^2)''.Cl^2$	,,	Sulphuric acid,	$(SO^2)''(HO)^2$
Chloride of phosphoryl,	$(PO)'''.Cl^3$	,,	Phosphoric acid,	$(PO)'''.(HO)^3$

α. Monatomic acid chlorides are mostly derived from organic acids; in fact, the only inorganic compounds of this class are *hydrochloric acid*, HCl; *chloride of azotyl*, NO.Cl, produced by the direct combination of chlorine and nitric oxide gases, or by the decomposition of nitromuriatic acid; and *chloride of nitryl*, $NO^2.Cl$, produced by the action of oxychloride of phosphorus on nitrate of lead: $3PbNO^3 + PCl^3O = Pb^3PO^4 + 3NO^2Cl$, or by the action of chlorhydrosulphuric acid upon nitre: $KNO^3 + HClSO^4 = NO^2Cl + KHSO^4$. Free chlorine, ClCl, may be regarded as the chloride corresponding to hypochlorous acid, Cl.HO.

The chlorides of monatomic organic acids are obtained: by the action of the chlorides of phosphorus, or of the oxychloride, on the corresponding acids:

$$\underset{\text{Benzoic acid.}}{C^7H^5O.H.O} + PCl^3.Cl^2 = \underset{\substack{\text{Chloride of}\\ \text{benzoyl.}}}{C^7H^5O.Cl} + HCl + PCl^3.O.$$

or of trichloride or oxychloride of phosphorus on salts of the same acids:

$$3(\underset{\substack{\text{Benzoate of}\\ \text{potassium.}}}{C^7H^5O.K.O}) + PCl^3O = K^3PO^4 + 3(\underset{\substack{\text{Chloride of}\\ \text{benzoyl.}}}{C^7H^5O.Cl}).$$

sometimes also by the action of chlorine on the corresponding hydrides (aldehydes):

$$C^7H^5O.H + Cl^2 = C^7H^5O.Cl + HCl.$$

They are mostly fuming volatile liquids (chloride of cyanogen, CN.Cl, is gaseous), remarkable for the facility with which they are decomposed by water and its derivatives (alcohols, alkalis, alkaline salts, &c.), and by ammonia and the compound ammonias.

Water transforms them into hydrochloric acid and a monobasic organic acid:

$$\underset{\substack{\text{Chloride of}\\ \text{acetyl.}}}{C^2H^3O.Cl} + H^2O = HCl + \underset{\text{Acetic acid.}}{C^2H^3O.H.O}.$$

With alkalis, in like manner, they yield the alkaline salts of the corresponding acids, and with alcohols, compound ethers:

$$\underset{\substack{\text{Chloride of}\\ \text{acetyl.}}}{C^2H^3O.Cl} + \underset{\text{Alcohol.}}{C^2H^5.H.O} = HCl + \underset{\text{Acetate of ethyl.}}{C^2H^3O.C^2H^5.O}.$$

Distilled with the alkaline salts of monobasic acids, they yield anhydrides:

$$\underset{\substack{\text{Chloride of}\\ \text{acetyl.}}}{C^2H^3O.Cl} + \underset{\substack{\text{Acetate of}\\ \text{potassium.}}}{C^2H^3O.K.O} = KCl + \underset{\substack{\text{Acetic}\\ \text{anhydride.}}}{(C^2H^3O)^2O}.$$

$$\underset{\substack{\text{Chloride of}\\ \text{acetyl.}}}{C^2H^3O.Cl} + \underset{\substack{\text{Benzoate of}\\ \text{potassium.}}}{C^7H^5O.K.O} = KCl + \underset{\substack{\text{Aceto-benzoic}\\ \text{anhydride.}}}{C^2H^3O.C^7H^5O.O}.$$

With ammonia, or carbonate of ammonium, they yield primary amides:

$$\underset{\substack{\text{Chloride of}\\\text{benzoyl.}}}{C^7H^5O.Cl} + NH^3 = HCl + \underset{\text{Benzamide.}}{N.H^2.C^7H^5O}.$$

and with compound ammonias they yield alkalamides:

$$\underset{\substack{\text{Chloride of}\\\text{benzoyl.}}}{C^7H^5O.Cl} + \underset{\substack{\text{Pheny-}\\\text{lamine.}}}{N.H^2.C^6H^5} = HCl + \underset{\text{Phenyl-benzamide.}}{N.H.C^6H^5.C^7H^5O}.$$

In like manner, with primary amides they form secondary amides:

$$\underset{\substack{\text{Chloride of}\\\text{benzoyl.}}}{C^7H^5O.Cl} + \underset{\text{Acetamide.}}{N.H^2.C^2H^3O} = HCl + \underset{\text{Aceto-benzamide.}}{N.H.C^2H^3O.C^7H^5O}.$$

β. *Diatomic acid chlorides*, derived from a double molecule of hydrochloric acid, and corresponding to dibasic acids. Such are:

Chloride of carbonyl (phosgene)	$(CO)''.Cl^2$
Chloride of sulphuryl	$(SO^2)''.Cl^2$
Chloride of succinyl	$(C^4H^4O^2)''.Cl^2$

Two volumes of the vapour of these chlorides contain 2 atoms of chlorine capable of conversion into a metallic chloride by the action of a mineral alkali.

They are obtained by the action of pentachloride of phosphorus on dibasic acids or anhydrides, the reaction, as shown by Williamson, consisting of two stages, the first resulting in the formation of a chlorinated acid, the second in that of a chloride, *e.g.* with sulphuric acid:

$$\left.\begin{matrix}(SO^2)''\\H^2\end{matrix}\right\}O^2 + PCl^2.Cl^3 = \underset{\substack{\text{Chlor-hydro-}\\\text{sulphuric acid.}}}{(SO^2)''\left\{\begin{matrix}HO\\Cl\end{matrix}\right.} + HCl + POCl^3.$$

$$(SO^2)''\left\{\begin{matrix}HO\\Cl\end{matrix}\right. + PCl^2.Cl^3 = \underset{\substack{\text{Chloride of}\\\text{sulphuryl.}}}{(SO^2)''.Cl^2} + HCl + POCl^3.$$

Chloride of sulphuryl and chloride of carbonyl are also formed by the direct combination of chlorine with the radicles, under the influence of light.

The diatomic acid chlorides are liquid at ordinary temperatures, with the exception of phosgene, which is gaseous. Their reactions are similar to those of the monatomic chlorides.

γ. *Triatomic Acid Chlorides*, corresponding to tribasic acids, and containing in two volumes of vapour, 3 vol. chlorine capable of conversion into a metallic chloride by the action of an alkali. Such are:

Trichloride of phosphorus	PCl^3
Chloride of phosphoryl (oxychloride of phosphorus) . .	$PO.Cl^3$
Chloride of sulphophosphoryl	$PS.Cl^3$
Chloride of boron	$B.Cl^3$
Chloride of cyanogen (solid)	$(CN)^3.Cl^3$

The trichlorides of arsenic and antimony must also be regarded as acid chlorides. The explosive compound, commonly called chloride of nitrogen, is perhaps also a trichloride, NCl^3; but, according to some authorities, it contains hydrogen.

Acid trichlorides are produced, for the most part, by the direct action of chlorine on the radicles. Chloride of phosphoryl is produced by the action of water, and of various derivatives of water, on the pentachloride, $PCl^5 + H^2O = 2HCl + POCl^3$; and chloride of sulphophosphoryl, in like manner by the action of sulphydric acid on the pentachloride. All these compounds are decomposed by water and its derivatives in the same manner as the mono- and di-atomic chlorides, yielding acids, salts, and compound ethers. Most of them unite with monatomic metallic chlorides, forming double chlorides.

δ. *Tetratomic Acid Chlorides*, containing 4 at. chlorine in 2 vols. of vapour. Some of the tetratomic metallic chlorides are of acid character, viz. $SnCl^4$ and $TiCl^4$; chloride of silicium, $SiCl^4$, is also tetratomic. The only organic compound of this class is tetrachloride of carbon, CCl^4 (p. 765). In these chlorides, two of the chlorine-atoms are retained less forcibly than the other two.

ε. *Pentatomic Acid Chlorides.*—Two only of these compounds are known, viz. PCl^5 and $SbCl^5$. They are both volatile, but the antimonic chloride suffers partial decomposition at the same time. To each of these chlorides there is a corresponding trichloride, and their general relations indicate that two of the chlorine-atoms are retained less forcibly than the other three.

With 1 at. of water, they yield hydrochloric acid and an oxychloride, *e.g.*:

$$PCl^5 + H^2O = 2HCl + PCl^3O,$$

but an excess of water likewise decomposes the oxychloride, forming hydrochloric acid and phosphoric or antimonic acid. Similar reactions are produced by alkalis, and in the case of pentachloride of phosphorus, by alcohols, the products being hydrochloric acid, a chloride of the alcohol-radicle, and either oxychloride of phosphorus or a phosphate of the radicle, according to the quantities present. Thus with phenylic alcohol:

$$PCl^5 + C^6H^5.H.O = C^6H^5.Cl + HCl + PCl^3O,$$

and

$$PCl^3O + 3(C^6H^5.H.O) = (C^6H^5)^3PO^4 + 3HCl.$$

With acids, or with salts of alkali-metal (acetate of sodium, for example) pentachloride of phosphorus yields oxychloride of phosphorus, hydrochloric acid, and a chloride of the acid radicle (pp. 898, 899), and in some cases, if a salt of the alkali-metal is present in excess, the corresponding anhydride is formed: thus

$$\underset{\text{Benzoate of sodium.}}{C^7H^5O.Na.O} + PCl^5 = PCl^3.O + NaCl + \underset{\text{Chloride of benzoyl.}}{C^7H^5O.Cl};$$

and

$$\underset{\text{Benzoate of sodium.}}{C^7H^5O.Na.O} + \underset{\text{Chloride of benzoyl}}{C^7H^5O.Cl} = NaCl + \underset{\text{Benzoic anhydride.}}{(C^7H^5O)^2O}.$$

CHLORINDATMITE. A product of the action of chlorine upon indigo (*q. v.*)

CHLORINDIN. See INDIN.

CHLORINE. *Symbol* Cl. *Atomic weight* 35·5. *Density* 35·5 (referred to hydrogen as unity.) *Atomic volume* 1.

Chlorine is a substance very widely distributed in nature. It exists chiefly in the form of chloride of sodium, which constitutes rock-salt when deposited in inland beds, sea-salt when dissolved in masses of water. The sea also contains chlorides of potassium, calcium, and magnesium. The chlorides of calcium, lead, mercury, and silver, respectively, form the partial or sole constituents of several well-known minerals, and free hydrochloric acid has been met with in the air of volcanic neighbourhoods. Chlorine was discovered by Scheele in 1774. Its elementary nature was first established by Davy in 1810.

1. Chlorine is usually prepared by the action of hydrochloric acid upon peroxide of manganese, at a gentle heat:

$$4HCl + Mn^2O^2 = 2H^2O + 2MnCl + Cl^2.$$

The liberated chlorine may be washed by transmission through a small quantity of water, and dried with oil of vitrol in the usual manner. It is best collected by downward displacement. It cannot be collected over mercury, on account of its rapid action on the metal. It cannot readily be collected over water, on account of solubility therein; but the difficulty may be obviated by evolving the gas rapidly, or by passing the delivery tube to the summit of the receiver, or by keeping the water in the trough perceptibly warm, or by saturating it with common salt. In the above reaction, the peroxide of manganese may be replaced by acid chromate of potassium; as also, though with questionable advantage, by several other oxidising agents, such as red or brown oxide of lead, chlorate of potassium, hypochlorite of calcium, nitric acid, &c. Moreover, a mixture of common salt and oil of vitrol, which generates hydrochloric acid abundantly, may be, and frequently is, substituted for the ready formed hydrochloric acid, thus:

$$2NaCl + 2H^2SO^4 + Mn^2O^2 = Na^2SO^4 + Mn^2SO^4 + 2H^2O + Cl^2.$$

This is the method usually adopted on the large scale, to generate chlorine for the manufacture of bleaching powder, chlorate of potassium, &c. It has the advantage of eliminating the whole of the chlorine from the chlorine-compound used, whereas, in the decomposition of the peroxide by hydrochloric acid alone, half the chlorine remains as protochloride of manganese. The sulphuric acid, when present in excess, has also the effect of drying the chlorine. The materials are mixed in a large alembic of nearly spherical form, and constructed either entirely of lead, surrounded at its lower part with a cast-iron steam-jacket, or of two hemispheres joined together in the middle, the upper being of lead, the lower of iron. In the former case the vessel is heated by steam, in the latter over a very gentle open fire. (See *Ure's Dictionary of Arts, Manufactures and Mines*, i. 666.)

Another method, which may be economically practised in sulphuric acid works, consists in heating a mixture of common salt and nitrate of sodium (Chili saltpetre) with excess of sulphuric acid. Hydrochloric and nitric acids are thereby evolved, and by their mutual action generate chlorine, peroxide of nitrogen and water:

$$HCl + HNO^3 = Cl + NO^2 + H^2O.$$

The mixed vapours are made to pass into condensers containing sulphuric acid, which absorbs the peroxide of nitrogen, forming a peculiar compound, which is afterwards used in the manufacture of sulphuric acid itself (see SULPHURIC ACID), while the chlorine passes on and may be used for the preparation of chlorates or hypochlorites. The residue of acid sulphate of sodium, left by the action of the sulphuric acid on the mixture of nitre and salt, remains liquid, and may be run off into a furnace and heated with an additional quantity of salt, producing hydrochloric acid and neutral sulphate of sodium, which last may be used in the manufacture of soda. (*Traité de Chimie générale, par Pelouze et Frémy*, 3^{me} éd. i. 414.)

2. Chlorine is also liberated by the simple action of a red heat upon certain chlorides, such as those of palladium, platinum, and gold, thus: $PtCl^2 = Pt + Cl^2$. Pentachloride of antimony, $SbCl^5$, breaks up, when gently heated, into trichloride of antimony, $SbCl^3$, and free chlorine, Cl^2; and in like manner, the trichloride of gold, $AuCl^3$, breaks up into protochloride of gold, $AuCl$, and free chlorine, Cl^2. Moreover, chlorine gas frequently results from the decomposition of its oxidised compounds.

Properties.—Chlorine has a yellowish-green colour, whence its name (χλωρος), and a pungent irritating smell. It is irrespirable unless very much diluted. It is one of the heaviest substances that are gaseous at common temperatures, being 35½ times heavier than hydrogen, and 2½ times heavier than atmospheric air. By a pressure of four atmospheres, at mean temperature 15·5° C., it is condensed into a yellow mobile liquid, having a specific gravity 1·33. It has resisted all attempts at solidification. At ordinary temperatures, water dissolves about twice its volume of chlorine, forming a solution which has the colour, smell, and general chemical properties of the gas. At low temperatures, water dissolves a still greater proportion of chlorine, and at the temperature 0° C. a definite hydrate of chlorine, $Cl.5H^2O$, crystallises out. If this hydrate be gently warmed in a sealed tube, it will, at a temperature of 38° C., decompose into a layer of water floating over a layer of liquid chlorine. This liquid chlorine may be readily distilled off, and condensed by means of a freezing mixture at the other extremity of the tube, which is usually bent for this purpose at an obtuse angle.

Chlorine possesses very active chemical properties, and gives origin to many phenomena of combination, substitution and indirect oxidation. It is moreover, non-inflammable, and does not unite directly with oxygen under any circumstances. At ordinary temperatures, chlorine combines directly with all the *metals*, with many metalloïds, such as *hydrogen* and *phosphorus*, and with many compound bodies, such as *sulphurous anhydride*, SO^2, *olefiant gas*, C^2H^4, *benzene*, C^6H^6, and *carbonic oxide*, CO. Its union with phosphorus, and with finely divided arsenic, antimony, tin, or copper, is attended with the phenomena of combustion. At increased temperatures, chlorine combines with many other substances, such as *sulphur*, *selenium*, *boron*, and *silicon*. It has not been made to combine directly with *carbon*. When ordinary combustible bodies containing carbon and hydrogen, such as paper, wood, wax-taper, &c., are ignited and immersed in a vessel of chlorine, the combustion continues chiefly at the expense of the hydrogen, which forms hydrochloric acid, while the carbon is deposited as a dense black smoke. Previous ignition of the hydrocarbonised substance is not always necessary to induce these phenomena. Paper dipped in oil of turpentine, $C^{10}H^{16}$, and plunged in a vessel of the gas, takes fire spontaneously, yielding abundance of hydrochloric acid and carbon.

Chlorine displaces *bromine*, *iodine*, and *fluorine*, from their combinations, by equivalent substitution. Free iodine strikes a deep blue colour with starch; and when starched paper dipped in iodide of potassium solution is brought into contact with chlorine, the iodine is liberated by the chlorine, and the characteristic blue iodide of starch produced: $KI + Cl = KCl + I$. Chlorine also displaces *hydrogen* by equivalent substitution, one half of the chlorine taking the place of an equivalent quantity of hydrogen, while the other half unites with the hydrogen eliminated:

$$\underset{\text{Salicin.}}{C^{13}H^{18}O^7} + Cl^2 = \underset{\text{Chloro salicin.}}{C^{13}H^{17}ClO^7} + HCl.$$

$$\underset{\text{Acetic acid.}}{C^2H^4O^2} + Cl^6 = \underset{\text{Trichloracetic acid.}}{C^2HCl^3O^2} + 3HCl.$$

Chlorine, by combining with hydrogen or a metal, acts indirectly as an oxidising agent. Thus, when chlorine-water is exposed to the action of sunlight, we have $Cl^2 + H^2O = 2HCl + O$. Again, when ferric hydrate, suspended in solution of hydrate of potassium, is treated with chlorine, we have produced ferric and hydrochloric acids, which react with the alkali to form potassium salts:

$$H^2O + \underset{\text{Ferric hydrate.}}{Fe^2H^3O^3} + Cl^3 = H^2O.Fe^2O^3, \ (i.e.\ \underset{\text{Ferric. acid.}}{H^2Fe^2O^4}) + 3HCl.$$

Chlorine destroys the colour of most organic pigments. This bleaching action is usually accompanied by oxidation and substitution, thus:

$$\underset{\text{Indigo.}}{C^8H^5NO} + H^2O + Cl^4 = \underset{\text{Chlorisatin.}}{C^8H^4ClNO^2} + 3HCl.$$

Chlorine also destroys odours of various kinds, and possibly infectious miasmata, either by abstracting hydrogen with or without substitution, or by indirectly oxidising.
W. O.

Antichloristic Theory.—Chlorine was originally regarded as a compound body, namely, *Oxygenised muriatic acid*, or *Oxymuriatic acid*. Muriatic acid was supposed to be a compound of oxygen with the unknown radicle *Muriaticum*, or *Murium*, and chlorine or oxygenised muriatic acid was supposed to contain the same radicle united with a larger quantity of oxygen. Moreover, as the driest muriatic acid, when brought in contact with red-hot metals, evolves a large quantity of hydrogen, and as 1 vol. of dry chlorine with 1 vol. of dry hydrogen forms 2 vols. of perfectly dry muriatic acid gas, it was concluded that 1 vol. of chlorine (or oxymuriatic acid), contains a half volume of oxygen, which, in the formation of muriatic acid gas, combines with 1 vol. of hydrogen; and that muriatic acid gas is an intimate compound, in equal numbers of atoms, of water, and a not yet isolated anhydrous muriatic acid, which may be called *hypothetical anhydrous muriatic acid*, to distinguish it from ordinary dry muriatic acid gas. Berzelius formerly arranged the various degrees of oxidation in the series as follows:

1 at. Murium=11·4 takes up of oxygen (=8)		and forms therewith	Antichloristic Names.	Chloristic Names.
2 at. = 16	. . .	27·4 pts. of	Hyp. anhyd. muriatic acid.	
3 „ = 24	. . .	35·4 „	Oxymuriatic acid.	Chlorine.
4 „ = 32	. . .	43·4 „	Euchlorine.	Hypochlorous anhydride.
6 „ = 48	. . .	59·4 „	?	Perchloric oxide.
8 „ = 64	. . .	75·4 „	Hyperoxymuriatic acid.	Chloric anhydride (hyp.)
10 „ = 80	. . .	91·4 „	?	Perchloric anhydride (hyp.)

It is easy to see that most of the phenomena exhibited by chlorine-compounds, may be rationally expressed in the language of this so-called "antichloristic theory." Muriatic acid gas is supposed to be a compound of 1 at. hypothetical anhydrous muriatic acid = 27·4 with 1 at. water = 9, making together 36·4 ($MuO^2.HO$).* Metallic chlorides are hypothetical anhydrous muriates of metallic oxides, $MuO^2.RO$, and may be formed, with evolution of hydrogen, by contact of a metal with muriatic acid gas, the oxidation of the metal being produced by the water. The same compounds are formed when a metal is immersed in oxymuriatic acid gas (MuO^3), the metal then taking away the third atom of oxygen of that gas, and forming an oxide, which unites with the remaining hypothetical anhydrous muriatic acid. The formation of a muriate and hyperoxymuriate (chlorate), when oxymuriatic acid comes in contact with the aqueous solution of an alkali, is effected by 5 at. of oxymuriatic acid giving up their third atom of oxygen to a sixth atom of the same acid, which is thereby converted into hyperoxymuriatic acid [$6MuO^3 + 6KO = KO.MuO^8 + 5(KO.MuO^2)$]. And in all cases in which chlorine is as an oxidising agent, where the one theory supposes that the element chlorine unites with hydrogen as a metal, and sets oxygen free, the other supposes that the third atom of oxygen in MuO^3, performs the same functions.

On the same theory, phosgene gas (oxychloride of carbon), is supposed to be a compound of hypothetical anhydrous muriatic acid with carbonic acid ($MuO^2.CO^2$); terchloride of phosphorus is a muriate of phosphorous acid, $PO^3.3MuO^2$, and the pentachloride is $PO^5.5MuO^2$, both compounds being formed by the combustion of phosphorus in the third atom of oxygen of MuO^3, whereby phosphorous or phosphoric acid is produced, which unites with the resulting MuO^2.

Such was the theory of the chlorine-compounds which maintained its ground till 1809. In that year, however, Gay-Lussac and Thénard showed, by arguments founded on numerous experiments, that the chemical relations of the so-called oxymuriatic acid, or chlorine, might all be explained on the supposition that it is an elementary substance, and this view was further carried out by Sir H. Davy in 1810, who first gave to this substance the name of CHLORINE. It is not necessary to go into all the arguments by which this view was ultimately established; it is sufficient to observe, that chlorine has never been shown to contain oxygen, or indeed to be capable in any way of resolution into simpler forms of matter, and therefore that its claim to the title of an element rests on the same foundation as that of the other bodies at present regarded as elementary. (For further details, see *Gmelin's Handbook*, ii. 356, and *Ure's Dictionary of Chemistry*, 4th edition, p. 318.)

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* O = 8.

CHLORINE, DETECTION AND ESTIMATION OF. 1. *Reactions.*—Chlorine in the free state is recognised by its suffocating odour, its yellow-green colour, the bleaching action which it exerts on litmus, indigo, and other vegetable colours, and the deep blue colour which it produces with a mixture of starch and iodide of potassium. The aqueous solution exhibits the same characters.

Hydrochloric acid and solutions of metallic chlorides, either neutral or slightly acidulated with nitric acid, give with *nitrate of silver*, an immediate white curdy precipitate of chloride of silver, insoluble in hot nitric acid, easily soluble in ammonia; and with *mercurous nitrate*, a white curdy precipitate of mercurous chloride (calomel) insoluble in nitric acid and in ammonia, and turned black by ammonia. Both these reactions are extremely delicate. Solutions of chloride of sodium of various degrees of dilution, give with nitrate of silver and mercurous nitrate, the reactions indicated in the following table:

1 pt. chlorine in:	Nitrate of Silver.	Mercurous Nitrate.
100,000 pts. water	Slight turbidity.	Slight precipitate.
200,000 „ „	Immediate slight cloud.	Turbidity after a few minutes.
400,000 „ „	Very slight turbidity.	Very slight turbidity after some minutes.
800,000 „ „	Very faint opalescence.	Opalescence after some time.
1,600,000 „ „	Scarcely perceptible opalescence.	Scarcely perceptible opalescence after some time.

With solution of sal-ammoniac, the silver-solution behaves in a similar manner, and gives a perceptible cloud, even with 3,200,000 pts. of water; with the mercurous solution, the reaction ceases to be perceptible with 400,000 pts. of water to 1 pt. of chlorine. (Lassaigne, J. Chim. méd. viii. 518.)

The only salts which give with silver-solution a precipitate resembling the chloride, are bromides, iodides, and cyanides. Either of these salts is easily detected in presence of a chloride, viz. bromides and iodides by the colours of the bromine and iodine when set free, and by their reaction with starch-paste; cyanides by the formation of Prussian blue with ferroso-ferric salts; but the detection of small quantities of chlorine in presence of excess of either of the other salts, presents greater difficulty. Bromide, iodide, and cyanide of silver are all insoluble in cold nitric acid, and more or less soluble in ammonia. Iodine is, however, completely precipitated by nitrate of palladium, which does not precipitate chlorine: consequently the chlorine may be detected by adding nitrate of silver to the filtrate. The best mode of detecting a small quantity of a chloride in presence of excess of bromide, is to distil the dried salts with sulphuric acid and acid chromate of potassium, and pass the evolved red vapours into ammonia: if chlorine is present, chlorochromic acid will be evolved, and the liquid will be coloured yellow, from formation of chromate of ammonium; but if only bromine is present, it will remain colourless. Cyanide of silver dissolves with decomposition when boiled with strong nitric acid, and may thereby be separated from the chloride, which will remain undissolved.

As the greater number of metallic chlorides are soluble in water, the method of precipitation by nitrate of silver may be applied to them immediately. Cuprous chloride, and many oxychlorides which are insoluble in water, dissolve in nitric acid, and the chlorine contained in them may then be detected in the same manner. Oxygen-salts of chlorine, viz. the hypochlorites, chlorites, chlorates, and perchlorates, give off their oxygen when heated, and are reduced to chlorides: the reduction, excepting in the case of perchlorates, may also be effected by sulphurous acid. The chlorides of phosphorus and other non-metallic elements, are decomposed by water, yielding hydrochloric acid, in which the chlorine may then be detected by nitrate of silver. The chlorine in organic compounds is for the most part not immediately precipitated by nitrate of silver, only indeed when it may be said to exist as hydrochloric acid, namely, in combination with organic bases; from other organic compounds, as the chlorides of the alcohol- radicles, and the numerous class of compounds in which chlorine takes the place of hydrogen, it must first be separated, either by ignition with lime, or by heating the compound with nitric acid in a sealed tube (pp. 225, 247).

2. *Quantitative Estimation.*—Chlorine is always estimated as chloride of silver. If not present as hydrochloric acid or a metallic chloride, it must be reduced to that state by one of the methods just indicated. The solution is then slightly acidulated with nitric acid in the cold (the application of heat to the acid solution would drive off part of the chlorine); nitrate of silver is added in excess; and the

liquid either briskly agitated with the precipitate, or else left for some hours in a warm place, till the precipitate has completely settled down. The precipitate is collected on a filter, which should be as small as possible, washed with water, and dried at 100° C. It must then be separated as completely as possible from the filter, and introduced into a porcelain crucible previously weighed, the filter burnt to ashes outside the crucible, the ashes added to the contents of the crucible, and the whole strongly heated over a lamp till the chloride of silver is brought to a state of tranquil fusion, after which it is left to cool and weighed. It contains 24·74 per cent. chlorine. As a small portion of the chloride may be reduced by the organic matter of the filter during ignition, it is best, before weighing, to treat the cooled mass with a small quantity of nitric acid, in order to dissolve the reduced silver, then add hydrochloric acid, evaporate to dryness, fuse, and weigh. The quantity of chlorine introduced in this manner, will only be the equivalent of that which may have been lost by the previous reduction. The chloride of silver may also be collected on a weighed filter, and dried in an oil-bath at about 150° C.

The quantity of chlorine in a soluble chloride may also be estimated volumetrically, by precipitation with a standard silver-solution, a cubic centimetre of which contains 30·42 milligrammes of silver, corresponding to 10 milligrammes of chlorine.

Volumetric Estimation of Chlorine in Hypochlorites: CHLORIMETRY.—The value of the so-called "chlorides of lime, potash, and soda," which are mixtures of the hypochlorites, chlorides, and hydrates of the respective metals, depends upon the percentage of hypochlorite which they contain, or, what comes to the same thing, on the quantity of chlorine which they evolve when treated with an acid, thus:

$$2CaClO + H^2SO^4 = Ca^2SO^4 + H^2O + Cl^2$$

and this quantity may be conveniently estimated: *a.* By the quantity of *arsenious anhydride* which it will convert into arsenic anhydride in an acid solution: $As^2O^3 + Cl^4 + 2H^2O = As^2O^5 + 4HCl$.—*b.* By the quantity of *ferrous oxide* which it will convert into ferric oxide.—*c.* By the quantity of *iodine* which it will liberate from a standard solution of iodide of potassium.

a. 14 grammes of pure arsenious anhydride, dried at 100° C., are dissolved in caustic potash, and the solution is diluted to 1 litre; 1 cub. cent. of this solution contains 0·014 grm. As^2O^3, and requires for its conversion into arsenic anhydride, 0·010 grm. chlorine ($As^2O^3 = 198 : Cl^4 = 142 :: 14 : 10$).

Five grms. chloride of lime are triturated with water, the whole washed into a graduated cylinder and diluted to 100 c.c.; 50 c.c. of the arsenious solution are placed in a beaker, diluted with water, saturated with hydrochloric acid, and coloured blue by a drop of indigo-solution; and the solution of chloride of lime (well shaken up), is added from a burette, till the blue colour is nearly destroyed. A fresh drop of indigo is now to be added, and then the chlorine-solution again, very cautiously, and drop by drop, the contents of the beaker being continually agitated, till the colour finally disappears. This marks the end of the operation: for the decoloration of the indigo does not take place till all the arsenious anhydride is converted into arsenic anhydride. The percentage of available chlorine in the sample is then easily calculated. Suppose that 45 c.c. of the arsenious solution have been employed; these correspond to 0·45 grm. chlorine: consequently, the sample contains 9 per cent. of chlorine in the form of hypochlorite.

Another mode of proceeding is to act on a known volume of a standard *alkaline* solution of arsenious anhydride added in excess, and to estimate the excess by a standard solution of iodine (p. 266). This, according to Mohr, is the only accurate method.

b. A weighed quantity of the sample is made to act on a known quantity of ferrous sulphate added in excess, and the quantity of that salt unoxidised by the hypochlorite, is estimated by a standard solution of permanganate of potassium. Every 1 at. ferrous oxide converted into ferric oxide, corresponds to 1 at. chlorine:

$$2Fe^2O + Cl^2 + H^2O = Fe^4O^3 + 2HCl.$$

c. For the iodometric method, see ANALYSIS, VOLUMETRIC (p. 266. On CHLORIMETRY, see also *Ure's Dictionary of Arts, Manufactures and Mines*, i. 671).

3. *Separation of Chlorine from other Elements.*—The method of precipitation by nitrate of silver serves to separate chlorine from all other elements except bromine and iodine.

To estimate chlorine in presence of *bromine*, the two elements are precipitated together by nitrate of silver, the precipitate dried, ignited, and weighed in the manner just described (p. 904), and the bromine determined by the method given at page 678. From this the quantity of bromide of silver in the precipitate is found by the proportion Br : AgBr = 80 : 188; this deducted from the total weight of the precipitate, gives the quantity of chloride of silver therein; and 24·74 per cent. of this last quantity is the amount of chlorine sought.

The method of estimating chlorine in presence of *iodine* is precisely similar.

When chlorine, bromine, and iodine occur together, the iodine is first precipitated by nitrate of palladium (see IODINE), and in the filtrate the chlorine and bromine are determined as above. Or the three elements may be separated and estimated by Field's method (p. 678).

4. *Atomic Weight of Chlorine.*—The atomic weight of chlorine was determined by Berzelius (Ann. Ch. Phys. [2] xci. 102) in connection with those of silver and potassium; and the same method has been carried out, with very nearly accordant results, by Marignac (J. pr. Chem. xxxi. 272; Ann. Ch. Pharm. xliv. 14), Penny (Phil. Trans. 1839, p. 129), Maumené (Ann. Ch. Phys. [3] xviii. 41; Ann. Ch. Pharm. lx. 173), and, lastly, by Stas (*Recherches sur les Rapports réciproques des Poids atomiques*, Bruxelles, 1860). The series of operations is as follows:

1. Chlorate of potassium, $KClO^3$, when heated to redness, gives off all its oxygen, leaving chloride of potassium, whence the atomic weight of chloride of potassium compared with that of oxygen is known.

2. As 1 at. chloride of potassium throws down 1 at. of silver from its solutions, the determination of the quantity of chloride of silver precipitated by 1 at. chloride of potassium gives the atomic weight of chloride of silver, AgCl.

Or if a known weight of silver be dissolved in nitric acid, and the quantity of chloride of potassium required to precipitate it be determined, the ratio between the atomic weights of silver and chloride of potassium becomes known; whence also the atomic weight of chlorine may be found, by determining the weight of chloride of silver produced from a given quantity of silver.

3. The quantity of chloride of silver (c) produced from a given weight of silver (s) is found, either by igniting silver in chlorine gas, or by dissolving it in nitric acid and precipitating by hydrochloric acid: hence, the atomic weight of chloride of silver (w) being previously known, that of silver (x), is found by the proportion, $c : s = w : x$, and that of chlorine by difference; or, the atomic weight of silver being found from the quantity of chloride of potassium required to precipitate it, that of chlorine is calculated from the composition of the chloride as just determined.

1. *Determination of the Amount of Oxygen in Chlorate of Potassium.*—This may be determined either by heating the salt to redness, or else by reducing it with hydrochloric acid, evaporating to dryness, and igniting. In carrying out the former method, it is necessary to arrange the apparatus in such a manner that any small particles of the salt that may be carried away by the escaping gas may be collected and weighed.

The proportions of oxygen and chloride of potassium in 100 pts. of the chlorate, and the atomic weight of chloride of potassium thence determined, by the proportion $O^3 : KCl = 48 : x$, are as follows, according to the authorities above quoted:

	Berzelius.	Marignac.	Penny.	Maumené.	Stas.
O^3	39·150	39·161	39·177	39·209	39·154
KCl	60·850	60·839	60·823	60·791	60·846
	100·000	100·000	100·000	100·000	100·000
Atomic weight of KCl .	74·606	74·575	74·520	74·424	74·59

2. *Determination of the Atomic Weight of Chloride of Silver:*

100 pts. of chloride of potassium yielded, by precipitation with nitrate of silver:

	Berzelius.	Marignac.	Maumené.
Chloride of silver	192·4	192·35	192·75

100 pts. of silver dissolved in nitric acid, require of KCl for precipitation:

Marignac.	Stas.
69·062	69·103

Now 1 at. chloride of potassium precipitates 1 at. silver, forming 1 at. chloride of silver; hence, according to Marignac—

$$100 : 192{\cdot}35 = 74{\cdot}575 : AgCl = 143{\cdot}44.$$

3. By igniting 100 pts. of silver in chlorine gas, the following quantities of chloride of silver are obtained:

	Berzelius.	Marignac.		Penny.	Maumené.	Stas.
		(1844.)	(1845.)			
AgCl . .	132·75	132·73	132·84	132·84	132·73	132·845

Comparing now Marignac's first number, 132·73 (which agrees with that of Maumené and very nearly with that of Berzelius) with his determination of the atomic weight of chloride of silver above quoted, viz. 143·44, we find for the atomic weight of silver:

$$132{\cdot}73 : 143{\cdot}44 = 100 : Ag = 108{\cdot}06$$

whence: $Cl = 143{\cdot}44 - 108{\cdot}06 = 35{\cdot}38$

and: $K = 74{\cdot}575 - 35{\cdot}38 = 39{\cdot}19$

If, again, we start from the same atomic weight of KCl as before, viz. 74·575, and assume, according to Marignac's second determination (also that of Penny) that 100 pts. silver produce 132·84 pts. chloride; also that 100 pts. silver require for precipitation 69·062 KCl (Marignac), we arrive at the numbers in the left hand column of the following table; those in the right are found in like manner from the determinations of Stas:

Marignac.	Stas.
$Ag = \frac{100 \times 74{\cdot}575}{69{\cdot}062} = 107{\cdot}98$	$Ag = \frac{100 \times 74{\cdot}59}{69{\cdot}103} = 107{\cdot}94$
$Cl = \frac{107{\cdot}98 \times 32{\cdot}84}{100} = 35{\cdot}46$	$Cl = \frac{107{\cdot}94 \times 32{\cdot}845}{100} = 35{\cdot}45$
$K = 74{\cdot}575 - 35{\cdot}46 = 39{\cdot}12$	$K = 74{\cdot}59 - 35{\cdot}45 = 39{\cdot}14$

Dumas (Ann. Ch. Pharm. cxiii. 21), by igniting silver in chlorine gas, found that:

9·954 grm. silver gave 13·227 AgCl
19·976 „ „ 26·542 „

whence, taking the atomic weight of silver at 108 (a result deduced from the analyses of the nitrate by Marignac):

The first determination gives Cl = 35·512
The second „ „ Cl = 35·499
Mean = 35·5

This number 35·5, being also very near to the results above detailed, is generally adopted.

CHLORINE, HYDRATE OF. $Cl.5H^2O$.—When water is introduced into a vessel filled with chlorine, in quantity not exceeding 5 at. water to 1 at. chlorine, and the vessel is exposed for some days to a freezing temperature, a pale yellow translucent hydrate is formed, sometimes in arborescent crystalline masses, sometimes in needles and rhombic octahedrons. It may be sublimed from one part of the vessel to another. When gently heated in an open vessel, it is resolved into chlorine gas and aqueous solution of chlorine. At 38° C. in a sealed tube, it is resolved into aqueous chlorine and free liquid chlorine, which separates as a distinct stratum. The hydrate acts on ammonia, ammoniacal salts, and alcohol in the same manner as gaseous chlorine. (Faraday, *Quarterly Journal of Science*, xv. 71.)

CHLORINE, OXIDES, and **OXYGEN-ACIDS OF.** Chlorine forms four oxygen-acids, all of which may be regarded as oxides of hydrochloric acid, namely:

Hypochlorous acid	$HClO$	Chloric acid	$HClO^3$
Chlorous acid	$HClO^2$	Perchloric acid	$HClO^4$

They are obtained by the following processes:

1. Hypochlorous acid, $HClO$, is produced by oxidising hydrochloric acid with permanganic acid; and hypochlorite of potassium is formed, together with chloride, by passing chlorine into a cold solution of potash:

$$KHO + Cl^2 = KClO + KCl.$$

2. Solution of hypochlorous acid, $HClO$, especially at increased temperatures, is converted spontaneously into chloric acid, $HClO^3$, together with water, chlorine, and oxygen. Moreover the solution of an alkaline hypochlorite, when boiled for some time, breaks up into chlorate and chloride: $3KClO = KClO^3 + 2KCl$.

3. Chloric acid, $HClO^3$, when deoxidated by nitrous acid, yields chlorous acid, $HClO^2$; and conversely, chlorous acid, by its spontaneous decomposition, yields chloric acid and other products.

4. Chloric acid, $HClO^3$, when oxidated at the positive pole of a voltaic battery, yields perchloric acid, $HClO^4$. Moreover chlorate of potassium, when moderately heated, breaks up into perchlorate of potassium, chloride of potassium, and oxygen.

Hypochlorites, chlorites, chlorates, and perchlorates of alkali-metal, when strongly heated, are alike converted into chlorides by loss of oxygen.

The anhydride of a monobasic oxygen-acid is formed from two atoms of the acid by the loss of one atom of water. The chlorine-acids should therefore yield the following anhydrides:

Acids.		Anhydrides.	
$2HClO$	$- H^2O =$	Cl^2O	Hypochlorous
$2HClO^2$	$- H^2O =$	Cl^2O^3	Chlorous
$2HClO^3$	$- H^2O =$	Cl^2O^5	Chloric
$2HClO^4$	$- H^2O =$	Cl^2O^7	Perchloric

The first two anhydrides are tolerably well known, the last two have not yet been obtained. We are, however, acquainted with the corresponding iodic and periodic anhydrides, I^2O^5 and I^2O^7, respectively. By the reabsorption of an atom of water, one atom of each anhydride is reconverted into two atoms of the corresponding acid

$$Cl^2O + H^2O = 2HClO$$
$$Cl^2O^3 + H^2O = 2HClO^2$$
$$(I^2O^5 \text{ or}) \; Cl^2O^5 + H^2O = 2HClO^3 \; (\text{or } 2HIO^3)$$
$$(I^2O^7 \text{ or}) \; Cl^2O^7 + H^2O = 2HClO^4 \; (\text{or } 2HIO^4)$$

In addition to the above anhydrides, a complete series of chlorine-oxides should obviously include three other terms, thus:

Cl^2	Chlorine	Cl^2O^4	Perchloric oxide
Cl^2O	Hypochlorous anhydride	Cl^2O^5	Chloric anhydride
Cl^2O^2	Chloric oxide ?	Cl^2O^6	Hyperchloric oxide ?
Cl^2O^3	Chlorous anhydride	Cl^2O^7	Perchloric anhydride

Soubeiran obtained from euchlorine (p. 913) a gas which decomposed into equal volumes of chlorine and oxygen, a result considered by Berzelius to be conclusive of the existence of chloric oxide. Hyperchloric oxide is not improbably identical with Millon's perchloro-chloric acid, Cl^6O^{17}, or $3Cl^2O^6$ (?) Perchloric oxide is a very well-known substance, which, moreover, appears to be identical with Millon's chloro-chloric acid, Cl^6O^{13}, or $3Cl^2O^4$ (?) Perchloric oxide is decomposed by water into chlorous and chloric acids:

$$Cl^2O^4 + H^2O = HClO^2 + HClO^3.$$

Hypochlorous Anhydride, Acid, and Salts.

HYPOCHLOROUS ANHYDRIDE. Cl^2O.—This gas, which was discovered by Balard in 1834 (Ann. Ch. Phys. [2] lvii. 225), may be prepared: 1. By adding glacial phosphoric acid to a concentrated solution of hypochlorous acid standing over mercury. The glacial phosphoric acid abstracts water from the hypochlorous acid, and the gaseous anhydride thus produced collects in the upper part of the tube: $2HClO - H^2O = Cl^2O$.

2. By passing chlorine gas over mercuric oxide contained in a tube kept cool by ice:

$$Hg^2O + Cl^4 = Cl^2O + 2HgCl.$$

The mercuric oxide should be prepared by precipitation, and dried at a somewhat high temperature, 300° C. Any excess of mercuric oxide remains combined with the resulting mercuric chloride in the form of a brown crystalline oxychloride. The gas may be collected by downward displacement, or in the mercurial trough, but it cannot be kept long over mercury, as it gradually acts upon the metal.

Hypochlorous anhydride is a gas of a pale reddish-yellow colour, and a powerful odour somewhat resembling that of chlorine. Its specific gravity does not appear to have been determined experimentally. By calculation, supposing the molecule to occupy two volumes, it is $\frac{2 \times 35{\cdot}5 + 16}{2} = 43{\cdot}5$, referred to hydrogen, and 3·015 referred to air as unity. It is so readily decomposed into two volumes of chlorine and one volume of oxygen, that it cannot be preserved unchanged, even for a few hours. By a slight elevation of temperature, or sometimes spontaneously, decomposition takes place with explosion. In sunlight the decomposition is very rapid, but usually tranquil. At the low temperature produced by a mixture of salt and ice, the gas is condensed into a deep orange-coloured liquid, heavier than water, and very explosive. Both the gaseous and liquid anhydride dissolve in water, undergoing decomposition and being converted into hypochlorous acid:

$$Cl^2O + H^2O = 2HClO.$$

The general reactions of the anhydride correspond with those of the acid, but are more violent.

HYPOCHLOROUS ACID. $HClO$.—This acid may be prepared:

1. From the anhydride, as just mentioned.
2. By passing air saturated with hydrochloric acid through a solution of perman-

ganate of potassium, acidulated with sulphuric acid and heated in a water bath. The distillate is a solution of hypochlorous acid formed by the direct oxidation of hydrochloric acid: $HCl + O = HClO$.

3. By the addition of almost any oxacid to a metallic hypochlorite.

4. By passing chlorine gas into water, holding suspended or dissolved certain metallic oxides, hydrates, carbonates, sulphates, phosphates, &c. In practice, oxide of mercury, and, according to Williamson, carbonate of calcium, are found to be the most advantageous. Either of these substances is to be agitated with water and treated with chlorine gas:

$$Ca^2CO^3 + H^2O + Cl^4 = CO^2 + 2HClO + 2CaCl.$$

The product of the action is to be distilled off, and if necessary concentrated by one or two redistillations of the most volatile distillates.

Aqueous hypochlorous acid has a yellowish colour, an acrid taste, and a characteristic sweet chloroïd smell. The strong acid decomposes rapidly, even when kept in ice. The dilute acid is more stable, but is decomposed by long boiling into chloric acid, water, chlorine, and oxygen. Hypochlorous acid, like chlorine, possesses powerful bleaching properties. Moreover, chloro-derivatives may be produced by its agency, thus:

$$\underset{\text{Benzene.}}{C^6H^6} + HClO = \underset{\text{Chlorobenzene.}}{C^6H^5Cl} + H^2O.$$

Hydrochloric acid decomposes hypochlorous acid, with formation of chlorine:

$$HClO + HCl = H^2O + Cl^2.$$

Hypochlorous acid is a very powerful oxidising agent. It rapidly converts many of the elements, iodine, selenium, and arsenic, for instance, into their highest oxides, at the same time liberating chlorine. The metals differ much from one another in the nature of their respective reactions with hypochlorous acid. Those which decompose the acid form oxides, as does iron, or oxychlorides, as do copper and mercury. Silver, indeed, forms a chloride and liberates oxygen, thus:

$$Ag^2 + 2HClO = 2AgCl + H^2O + O.$$

Many metallic oxides, those of manganese, cobalt, and lead, for example, are peroxidised, with liberation of chlorine; but oxide of silver is converted into chloride of silver, with liberation of oxygen:

$$Ag^2O + 2HClO = 2AgCl + H^2O + O^2.$$

HYPOCHLORITES.—1. Pure hypochlorites are made by neutralising hypochlorous acid with hydrates, such, for instance, as those of sodium, potassium, calcium, barium, magnesium, zinc, copper, &c.—2. Hypochlorites are usually prepared by passing chlorine gas into solutions of hydrated or carbonated alkali, or over the dry hydrates of the earths. By this process, a chloride and a hypochlorite are simultaneously produced. The reaction is believed to be as follows:

$$Cl^2 + 2CaHO = CaCl + CaClO + H^2O.$$

These mixed compounds constitute the bleaching and disinfecting salts of commerce, the properties of which were known as early as the time of Berthollet. They were long regarded as chlorides of the alkali- and earth-metals, and known as *chloride of lime*, *chloride of soda*, &c., till Berzelius suggested the idea that they might be mixtures of metallic chlorides with alkaline chlorites ($M^2O.Cl^2O^3$). Balard, in 1834, showed that their properties are best explained by regarding them as mixtures of chlorides and hypochlorites. The only objections to this view are that alcohol does not extract chloride of calcium from bleaching powder, as we should *à priori* expect, and, unlike mixtures containing chloride of calcium, bleaching powder is not deliquescent. These anomalies may possibly be due to the formation of a double salt, containing chloride and hypochlorite of calcium in chemical combination with one another.

The pure hypochlorites, when acted upon by sulphuric acid, or even by carbonic acid, liberate hypochlorous acid, thus:

$$2CaClO + H^2SO^4 = 2HClO + Ca^2SO^4.$$

The mixed salts behave in the same manner, provided the sulphuric acid is not in excess; but otherwise chlorine, and not hypochlorous acid, is evolved:

$$CaClO + CaCl + H^2SO^4 = H^2O + Cl^2 + Ca^2SO^4.$$

The sulphuric acid acts first upon the hypochlorite to liberate hypochlorous acid, and then upon the chloride to liberate hydrochloric acid, the co-existence of which two acids cannot occur, owing to their mutual decomposition into water and free chlorine, as we have already seen. Hydrochloric acid can liberate hypochlorous acid from the pure or mixed salts, thus: $NaClO + HCl = HClO + NaCl$. But any excess of hydrochloric acid immediately reacts upon the nascent hypochlorous acid to form water and chlorine. Solutions of the hypochlorites, either pure or commercial, are very unstable, but are more permanent in the presence of free alkali. They gradually give off oxygen gas, and finally yield mixtures of chloride and chlorate. Their decomposition takes place very definitely at a boiling temperature, thus:

$$3CaClO = CaClO^3 + 2CaCl.$$

Of themselves they act as bleaching agents, probably by evolution of oxygen; but the effects produced by acidifying their solutions, and thereby liberating hypochlorous acid, are much more rapid. With most metallic oxides and salts, the hypochlorites react as does hypochlorous acid upon the oxides. They convert oxide of silver, for instance, into chloride of silver, with liberation of oxygen:

$$Ag^2O + 2NaClO + H^2O = 2AgCl + 2NaHO + O^2;$$

and sulphate of manganese into hydrated peroxide of manganese, with liberation of chlorine:

$$Mn^2SO^4 + 2NaClO + H^2O = Na^2SO^4 + 2MnHO^2 + Cl^2.$$

The characters of the individual salts will be described in a distinct article (HYPOCHLORITES). For the valuation of hypochlorites see p. 904.

Chlorous Anhydride, Acid, and Salts.

CHLOROUS ANHYDRIDE. Cl^2O^3.—This gas, discovered by Millon (Ann. Ch. Pharm. xlvi. 298), results from the spontaneous decomposition of chlorous acid, which is a somewhat ill-defined and unstable substance:

$$2HClO^2 = H^2O + Cl^2O^3.$$

It is also produced by the reaction of chloric acid with nitrous acid or anhydride:

$$2HNO^2 + 2HClO^3 = 2HNO^3 + H^2O + Cl^2O^3.$$

Instead of preformed chloric acid and nitrous acid or anhydride, a mixture of chlorate of potassium, nitric acid, and arsenious anhydride is usually employed. The nitric acid is first reduced by the arsenious anhydride to the state of nitrous acid, which is the real deoxygenant of the liberated chloric acid:

$$As^2O^3 + 2H^2O + 2KClO^3 = 2KH^2AsO^4 + Cl^2O^3.$$

The reaction is effected by the application of a very gentle heat. The arsenious anhydride may be replaced by tartaric acid or other deoxidising agent. The gas must be collected by displacement.

Chlorous anhydride is a yellowish green gas, permanent in a freezing mixture of ice and salt, but liquefiable by extreme cold. Its specific gravity, calculated for a condensation to 2 vols., is $\frac{71 + 48}{2} = 59{\cdot}5$ referred to hydrogen, and 4·123 referred to air. At slightly elevated temperatures, 57° C. and upwards, it is decomposed, with explosion, into chlorine and oxygen. It dissolves freely in water or in solutions of the alkaline and earth-alkaline hydrates, gradually forming chlorous acid or chlorites.

CHLOROUS ACID. $HClO^2$.—This acid may be prepared by condensing chlorous anhydride in water:

$$Cl^2O^3 + H^2O = 2HClO^2.$$

or by acting upon a chlorite with some diluted acid, such as sulphuric or phosphoric:

$$2PbClO^2 + H^2SO^4 = 2HClO^2 + Pb^2SO^4.$$

The acid, or its concentrated solution, is a greenish yellow liquid of great tinctorial power, and having strong bleaching and oxidising properties. It does not decompose carbonates, but reacts slowly with caustic alkalis and earths to form chlorites.

CHLORITES. $MClO^2$.—The alkaline and earthy chlorites are formed as above described. They also result from the action of perchloric oxide on bases (p. 912). They are, for the most part, soluble, crystallisable, colourless salts, possessed of bleaching properties. The insoluble chlorites of silver, lead, and other metals are produced by double decomposition:

$$AgNO^3 + KClO^2 = KNO^3 + AgClO^2.$$

The chlorites are decomposed even by carbonic acid.

For the characters of the individual chlorites, see page 914.

Chloric Acid and Salts.

Chloric Acid. $HClO^3$. (Vauquelin, Ann. Chim. xcv. 91; Serullas, Ann. Ch. Phys. [2] xlv. 204, 270.)—1. The acid is liberated from chlorates by the addition of a stronger acid. It is found advantageous to use equivalent quantities of chlorate of barium and sulphuric acid:

$$2BaClO^3 + H^2SO^4 = 2HClO^3 + Ba^2SO^4.$$

The solution of chloric acid is separated from the insoluble sulphate of barium by filtration, and concentrated by evaporation in vacuo.—2. This acid also results from the spontaneous decomposition of solutions of hypochlorous acid, chlorous acid, and peroxide of chlorine.

Chloric acid is a colourless syrupy liquid, having a strong acid reaction, and when warm, a pungent chloroïd smell. It is decomposed by organic matter, with charring, and frequently even with ignition. It is somewhat unstable at ordinary temperatures. At 40° C. it undergoes marked decomposition, and at a boiling heat is rapidly converted into perchloric acid, water, chlorine, and oxygen. It is a very powerful oxidising and bleaching agent. It is decomposed by hydrochloric, sulphydric, and sulphurous acids, with liberation of chlorine.

Chlorates. $MClO^3$.—1. These salts may be prepared by saturating the acid with bases. Chlorate of barium is usually made by this process (p. 885).

2. Zinc, and one or two other metals, dissolve in chloric acid to form chlorates, thus: $HClO^3 + Zn = ZnClO^3 + H$; but a part of the acid always undergoes a more complex decomposition.

3. Alkaline chlorates are produced by boiling solutions of the hypochlorites, or, what comes to the same thing, by passing chlorine into caustic or carbonated alkali, and boiling the resulting liquid: $3KClO = KClO^3 + 2KCl$. The chlorate is separated from the chloride by crystallisation.

The chlorates are chiefly interesting as sources of oxygen gas. Chlorate of potassium and most chlorates are decomposed by heat into chloride and oxygen, thus, $KClO^3 = KCl + O^3$; but the chlorates of the earth-metals yield oxygen, chlorine, and metallic oxide: $2MgClO^3 = Mg^2O + Cl^2 + O^5$. Prior to the ultimate decomposition of chlorate of potassium, a portion of perchlorate is produced. The fused chlorates are powerful oxidising agents. Mixtures of chlorate with combustible substances, such as sulphur, sulphide of antimony, and sugar, explode violently on the application of heat, or by percussion. Strong sulphuric acid liberates perchloric oxide from the chlorates, and, by its action on mixtures of chlorate with combustible matters, frequently induces combustion. Nitric acid reacts with chlorate of potassium to form nitrate of potassium, perchlorate of potassium, and free chlorine and oxygen gases. Hydrochloric acid produces euchlorine, which is a gaseous mixture of chlorine and perchloric oxide. A mixture of chlorate of potassium and hydrochloric acid is much used for oxidising mineral and organic compounds. All the chlorates are soluble in water, and hence do not precipitate the salts of the heavy metals. Chlorate of potassium, the most important member of the class, is one of the least soluble. Unlike the hypochlorites and the chlorites, the chlorates do not bleach until after the addition of an acid. [For the description of the individual salts, see pp. 885—890].

Perchloric Acid and Salts.

Perchloric Acid. $HClO^4$.—This acid was discovered in 1815 by Count Stadion (Gilb. Ann. lii. 197), afterwards more particularly examined by Serullas (Ann. Ch. Phys. [2] xlv. 270; xlvi. 294, 323), and quite recently by Roscoe[*], who has obtained it in definite form. It is produced: 1. By the electrolysis of chloric acid. Oxygen and chlorine are evolved in small quantities at the positive pole, and hydrogen at the negative pole; but the greater part of the oxygen remains in the liquid, and converts the chloric into perchloric acid (Stadion).—2. By the distillation of chloric acid (p. 910).—3. By the action of sulphuric acid upon chlorate of potassium (see Perchloric Oxide, p. 912).—4. By the action of certain acids upon the perchlorates. Thus, fluosilicic may be added to perchlorate of potassium, and the resulting insoluble fluosilicate of potassium filtered off from the solution of perchloric acid; or sulphuric instead of fluosilicic acid may be employed, and the volatile perchloric acid distilled off from the sulphate of potassium. (Serullas.)

Aqueous perchloric acid obtained by either of these methods may be concentrated by boiling till it attains a temperature of 203° C., after which it passes over unchanged in the form of an oily liquid containing 70·3 per cent., $HClO^4$. If this oily acid be

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[*] These results, which are not yet published, have been kindly communicated by Professor Roscoe.

distilled with twice its volume of strong sulphuric acid, it gives up its water to the latter, and perchloric acid passes over nearly pure in the form of a yellowish strongly fuming liquid. On continuing the distillation, the oily acid above-mentioned begins to pass over; but as soon as it comes in contact with the more volatile portion of the distillate, the two unite into a crystalline mass consisting of a hydrate, $HClO^4.H^2O$. Both these products are, however, contaminated with sulphuric acid mechanically carried over. To obtain the volatile liquid in a pure state, the crystals must be redistilled *per se*. They then split up into pure perchloric acid, $HClO^4$, which is obtained as the first produce of the distillation, and the oily acid, which contains a larger proportion of water, and passes over afterwards. (Roscoe.)

Pure perchloric acid, $HClO^4$, is a colourless very volatile liquid, having a specific gravity of 1·782 at 15·5 C. Its vapour is likewise colourless and transparent, but on coming in contact with the air, it absorbs water, and forms dense white fumes. Perchloric acid in this state is one of the most powerful oxidising agents known; a single drop brought in contact with charcoal, paper, wood, or other organic substance, immediately causes an explosive combustion, which in violence does not fall far short of the sudden decomposition of chloride of nitrogen. The acid unites also very energetically with water, a violent hissing noise being produced. The greatest care must be taken in working with this substance, as one drop falling on the skin produces cauterisation, and leaves a wound which does not heal for months. Like pure nitric acid, this acid cannot be distilled by itself without undergoing decomposition, a singular black explosive body being produced when it is boiled. It likewise undergoes spontaneous decomposition at the ordinary temperature, the bulbs in which it was sealed exploding even when kept in the dark.

The composition of pure perchloric acid was determined by neutralising it with carbonate of potassium, adding acetic acid to acid reaction, evaporating to dryness, throwing the perchlorate of potassium on a weighed filter, washing out the soluble acetate with absolute alcohol, and determining the composition of the potassium salt thus produced. In this manner results agreeing closely with the theory were obtained. Thus, 1·2185 grm. of acid gave 1·6785 of potassium salt, calculation requiring 1·6876. Of this salt, 0·966 grm. heated with peroxide of iron lost 0·444 grm., and the residual KCl required 0·744 grm. pure silver for complete precipitation. Now 0·744 Ag is equivalent to 0·513 KCl, and by calculation 0·966 $KClO^4$ should yield 0·519 KCl. (Roscoe.)

The *Hydrate*, $HClO^4.H^2O$ (containing 84·81 per cent. $HClO^4$), is obtained in the pure state by adding water to the pure acid $HClO^4$. It is a white, solid, crystalline substance, which melts at 50° C., and undergoes decomposition when heated to 110°, splitting up into the pure acid and an aqueous oily acid. Its composition was determined by the method adopted in the case of the pure acid. The specific gravity of the liquid hydrate at 50° C. is 1·811. Although not so violent in its action on organic matter as the pure acid, the fused hydrate when brought into contact with paper or wood, induces immediate combustion, and when dropped into water, combines therewith making a hissing noise.

When it is distilled, the temperature is found to rise gradually to 203° C., at which point it remains constant, a heavy oily liquid then passing over, which in outward appearance cannot be distinguished from sulphuric acid. This acid contains 72·1 per cent. of $HClO^4$, and does not therefore correspond to any definite hydrate, $HClO^4.2H^2O$ requiring 73·6 per cent. $HClO^4$, and $HClO^4.3H^2O$, requiring 65·05 per cent. $HClO^4$. If aqueous perchloric acid be concentrated by boiling, water goes off, and the temperature rises to 200° C., when the acid is likewise found to contain 72·1 per cent. of $HClO^4$. Hence an aqueous acid loses water, and the crystallised hydrate loses perchloric acid on boiling under the ordinary atmospheric pressure, until both arrive at a point when no further change takes place, and an acid containing 72·1 per cent. $HClO^4$ passes off unchanged. (Roscoe.)

Aqueous perchloric acid reddens litmus strongly, but does not bleach. It dissolves zinc and iron, with evolution of hydrogen, forming perchlorates. When dilute, it is unaffected by sulphydric and sulphurous acids, which reduce all other oxacids of chlorine.

PERCHLORATES.—These salts are produced: 1. By the reaction of perchloric acid with metals, oxides, sulphides, or carbonates, or of perchlorate of barium with sulphates, thus:

$$HClO^4 + BaHO = BaClO^4 + H^2O$$
$$2BaClO^4 + Na^2SO^4 = 2NaClO^4 + Ba^2SO^4.$$

2. By the decomposition of chlorates. During the decomposition of chlorate of potassium by heat, and after a considerable evolution of oxygen has taken place, the previously fused salt is observed to assume a pasty condition, and if the heat be then discontinued, the residue will be found to consist principally of perchlorate and chloride of potassium,

which two salts may be separated from one another by solution and crystallisation, the perchlorate being much the less soluble:

$$2KClO^3 = KClO^4 + KCl + O^2.$$

Or, the chlorate of potassium may be decomposed by nitric acid:

$$3KClO^3 + 2HNO^3 = KClO^4 + 2KNO^3 + H^2O + Cl^2 + O^4,$$

and the resulting nitrate and perchlorate of potassium separated by crystallisation.

Perchlorate of potassium is sparingly soluble in cold water; but the perchlorates in general are soluble, crystalline, deliquescent salts. They deflagrate, though less violently than the chlorates, when thrown on ignited charcoal. They require a stronger heat than do the chlorates to effect their decomposition into chloride and oxygen. Sulphuric acid liberates perchloric acid from the perchlorates, but not until the temperature rises to 100° C.: other acids liberate perchloric acid, only when they form insoluble salts with the bases of the perchlorates. Hence, unlike chlorates, the perchlorates do not assume a yellow colour when acted upon by sulphuric or hydrochloric acid. [For the description of the individual salts, see PERCHLORATES.]

Perchloric Oxide and Euchlorine.

PERCHLORIC OXIDE. Cl^2O^4.—This very explosive compound, which was discovered by Count Stadion (*loc. cit.*), may be prepared by the action of strong sulphuric acid upon chlorate of potassium, whereby perchlorate of potassium, acid sulphate of potassium, water, and perchloric oxide are produced:

$$3KClO^3 + 2H^2SO^4 = KClO^4 + 2KHSO^4 + H^2O + Cl^2O^4.$$

The chlorate should be purified by recrystallisation, fused after drying, at the lowest adequate temperature, and then finely pulverised. The powder must be added little by little to sulphuric acid, made cool by a mixture of ice and salt, until a pasty mass is produced. This is to be set aside for some time, and afterwards, by means of a water-bath, to be very gently heated in a retort. The evolved gaseous perchloric oxide must be collected by downward displacement. Calvert has shown that perchloric oxide, mixed with carbonic acid, may be readily obtained by heating finely powdered chlorate of potassium with crystallised oxalic acid to a temperature of 70° C. (p. 888).

Perchloric oxide is a gas of a bright yellow colour, and sweet aromatic smell. At the low temperature produced by a mixture of salt and ice, it is condensed into a yellowish highly explosive liquid. Faraday succeeded in solidifying it by means of the intense cold produced by the evaporation of solid carbonic acid and ether. In daylight the gas undergoes spontaneous decomposition into chlorine and oxygen. This decomposition is frequently, and, when induced by elevation of temperature, almost invariably, attended by a violent explosion. The contact of highly combustible matters also determines an explosion. Liquid perchloric oxide unites with water at a temperature of 0° C., to form a solid hydrate. At ordinary temperatures, water dissolves several times its volume of the gas. The solution has a yellow colour, is devoid of acid reaction, bleaches powerfully, and is very unstable, being decomposed into chloric acid, chlorous acid, and other products. Perchloric oxide is absorbed by alkaline solutions, with formation of chlorate and chlorite:

$$2KHO + Cl^2O^4 = KClO^3 + KClO^2 + H^2O.$$

The molecule of perchloric oxide Cl^2O^4, like the molecule of chlorine Cl^2, seems to be binary or dyadic, and to halve itself in the act of combination. In this manner, the correlations of chlorite and chlorate would correspond with those of chloride and hypochlorite, thus:

$$\text{Chloride}\ \left.\begin{matrix}H\\Cl\end{matrix}\right\}\quad \text{Hypochlorite}\ \left.\begin{matrix}H\\Cl\end{matrix}\right\}O.\quad \text{Chlorite}\ \left.\begin{matrix}H\\ClO^2\end{matrix}\right\}\quad \text{Chlorate}\ \left.\begin{matrix}H\\ClO^2\end{matrix}\right\}O.$$

EUCHLORINE.—When chlorate of potassium is acted upon by hydrochloric acid, a bright yellow gas, called euchlorine, is liberated. This gas contains chlorine and oxygen in the same proportions as hypochlorous anhydride, Cl^2O, but despite its uniformity of composition, it is evidently a mixture, probably of chlorine and perchloric oxide. The following equation is believed to express its formation correctly:

$$4KClO^3 + 12HCl = 4KCl + 6H^2O + (9Cl + 3ClO^2).$$

This mixed gas has a sweet aromatic smell, and powerful bleaching properties. By passing it through a U-tube immersed in a mixture of salt and ice, the perchloric oxide is separated in the liquid state from the free uncondensed chlorine. According to Millon, the liquid perchloric oxide obtained by cooling euchlorine, differs from the liquid perchloric oxide obtained by means of sulphuric acid and chlorate of potassium, in its somewhat greater stability, in its somewhat higher boiling point, and in the circumstance that, although, like the normal compound, it is decomposed by alkalis into chlorate and chlorite, yet that, unlike the normal compound, it yields two equivalents of the former for one of the latter salt. Hence Millon assigns to it the formula $Cl^6O^{13} = 3Cl^2O^4$?

$$Cl^6O^{13} + 6KHO = 3H^2O + 4KClO^3 + 2KClO^2,$$

but these differences may probably be due to differences in the purity of these two bodies. Moreover, perchloric oxide is a very difficult subject to investigate, and the descriptions of different experimentalists vary considerably from one another. (See *Gmelin's Handbook*, ii. 304, 310.) W. O.

CHLORINE, SULPHIDES OF. Two only of these compounds are known in the free state, viz. SCl and SCl^2. The former is analogous in composition to hypochlorous anhydride, ClO, but exhibits no analogy whatever to that compound in its properties. It is doubtful indeed whether the sulphur or the chlorine in these compounds is the negative element; but they are usually regarded as *chlorides of sulphur*, and as such will be more fully considered. (See SULPHUR.)

Similar observations apply to the compounds of chlorine and selenium.

CHLORIODOFORM. *Dichlorinated Iodide of Methyl.* $CHCl^2I$. (Serullas, Ann. Ch. Phys. [2] xxv. 314; xxxix. 225.—Mitscherlich, Pogg. Ann. xi. 164.—Bouchardat, Ann. Ch. Pharm. xxii. 2229.—Gm. vii. 337). This compound was discovered by Serullas in 1824, but its composition was first correctly ascertained by Bouchardat. It is obtained by distilling iodoform with an equal weight of pentachloride of phosphorus or mercuric chloride. The materials are intimately mixed, and distilled in a retort; the dark red distillate is decolorised with aqueous potash, then shaken up with strong sulphuric acid, to free it from chloride of ethylene, afterwards separated from the sulphuric acid by a tap-funnel, and purified by rectification.

Chloriodoform is a transparent pale yellow liquid of specific gravity 1·96, having an aromatic odour and saccharine taste, and becoming rose-coloured by exposure to the air. It remains fluid at the lowest temperatures, and is not decomposed by distillation. It is but sparingly soluble in water. Heated with strong aqueous potash, or with alcoholic potash, it yields formate, chloride, and iodide of potassium:

$$CHCl^2I + 2K^2O = CHKO^2 + 2KCl + KI.$$

In contact with chlorine gas, it solidifies and yields trichloride of iodine.

CHLORISAMIC ACID and **CHLORISAMIDE.** See ISAMIC ACID and ISAMIDE.

CHLORISATIC ACID. See ISATIC ACID.

CHLORISATYDE and **CHLORISATYDIC ACID.** See ISATYDE and ISATIC ACID.

CHLORISATIN. See ISATIN.

CHLORISATOSULPHITES. See ISATOSULPHITES.

CHLORITE. *Leuchtenbergite, Pennine.*—This name is applied to certain silicates of magnesia and alumina occurring in plutonic formations, and forming the characteristic ingredients of chlorite slate. It formerly included ripidolite and clinochlore, and is still applied to at least two minerals, differing in crystalline form, and somewhat also in chemical composition. Chlorite from Achmatowsk in the Ural is monoclinic; but the variety called *Pennine*, from Zermatt in the Valais, is hexagonal, generally forming six-sided tables with perpendicular edges, oP . ∞ P, or with bevelled edges, oP . P, where P denotes a six-sided pyramid with basal edges of 106° 50′ and pyramidal edges of 132° 40′; also with other faces subordinate. Cleavage perfect, parallel to the base. The crystals are sometimes imbedded singly, but more frequently grouped in spherical, conical, or vermiform masses; also in minute scales, forming a deposit on other minerals. Specific gravity 2·65 to 2·85. Hardness 2·0 to 2·5. Flexible in thin laminæ, but not elastic. Colour various shades of green, from leek to blackish green. Small crystals are dichromatic, appearing red when viewed in a direction perpendicular to the vertical axis. Lustre nacreous on the basal faces, vitreous to waxy on the others. Transparent in thin laminæ, but generally translucent, and transparent on the edges only.

All varieties of chlorite give off water when heated in a tube, and melt with difficulty before the blowpipe to a black slag, sometimes magnetic. The mineral gives with fluxes the reactions of iron, more rarely that of chromium, and is perfectly decomposible by sulphuric acid.

The several varieties of chlorite exhibit considerable diversity of composition; the essential constituents are silica, alumina, magnesia, and water, the alumina, however, being often more or less replaced by ferric oxide and the magnesia by ferrous oxide. The following are analyses: 1. Varrentrapp (Pogg. Ann. xlviii. 185).—2. Kobell

(J. pr. Chem. xvi. 470).—3. **Brüel** (Pogg. Ann. xlviii.)—4. **Delesse** (Ann. Ch. Phys. [3] ix. 396).—5, 6. **Marignac** (*ibid.* x. 430).—7, 8. **Hermann** (J. pr. Chem. xi. 13).—9. **Schweizer** (Pogg. Ann. l. 526).—10, 11. **Marignac** (*loc. cit.*)

	SiO^2	Al^4O^3	Mg^2O	Fe^4O^3	Fe^2O	Mn^2O	H^2O
1. Achmatowsk .	30·38	16·96	33·97	—	4·37	—	12·63 = 98·31
2. Schwarzenstein .	32·68	14·57	33·11	—	5·97	0·28	12·10 insol. 1·02 = 99·73
3. Zillerthal . .	31·47	16·67	32·56	—	5·97	0·01	12·42 = 99·11
4. Pyrenees . .	32·1	18·5	36·7	—	0·6	—	12·1 = 100
5. Ala (Piedmont) .	30·01	19·11	33·15	4·81	—	—	12·53 = 99·60
6. Slatoust (Ural) .	30·27	19·85	33·13	4·42	—	—	12·54 = 100·25
7. " *white* .	30·80	17·27	37·07	1·37	—	—	12·30 = 98·82
8. *Leuchtenbergite* .	32·35	18·00	32·29	4·37	—	—	12·50 = 99·51
9. Zermatt (*Pennine*)	33·07	9·69	32·34	—	11·36	—	12·58 = 99·08
10. " "	33·36	13·24	34·21	5·93	—	—	12·80 Cr^2O^3 0·20 = 99·74
11. Binnen "	33·95	13·46	33·71	6·12	—	—	12·52 " 0·24 = 100

These numbers may be approximately represented by the formula $2(3M^2O.SiO^2) + Al^4O^3.SiO^2 + 4aq.$ which, if M denotes magnesium, requires 30·82 SiO^2, 17·14 Al^4O^3, 40·03 Mg^2O, and 12·01 water. If alumina be represented as a protoxide (by substitution of $al = \frac{2}{3}$ Al), the preceding formula may be reduced to the form $M^2O.M^4SiO^4 + \frac{2}{3}aq.$ Besides the above localities, chlorite is found on the Col de Pertuis, in the Vosges, and in various parts of the Eastern United States. (Dana, ii. 294; *Rammelsberg's Mineralchemie*, p. 534; Handw. d. Chem. 2^{te} Aufl. ii. [2] 1106.)

Chlorite Earth is earthy chlorite in the older sense of the word, without regard to the distinction between chlorite and ripidolite, because in the earthy state the two minerals can scarcely be distinguished.

Chlorite Ferruginous. *Delessite.*—This mineral occurs in the amygdaloïdal porphyry of Oberstein and Zwickau. It is massive, with short fibrous or scaly feathery texture. Specific gravity 2·89. Hardness 2·5. Colour olive-green to blackish-green. According to Delesse (Ann. Min. [4] xvi. 520) it contains 29·45 per cent. SiO^2, 18·25 Al^4O^3, 8·17 Fe^4O^3, 15·12 Fe^2O, 15·32 Mg^2O, 0·45 Ca^2O, and 12·57 water (= 99·33), which may be approximately represented by the general formula $2(2M^2O.M^4O^3.2SiO^2) + 5aq.$ *Grengesite*, from Grengesberg in Dalecarlia, containing, according to Hisinger, 27·01 SiO^2, 14·31 Al^4O^3, 2·18 Mn^4O^3, 25·63 Fe^2O, 14·31 Mg^2O, and 12·53 water, appears to be related to it. (Dana, ii. 296; *Rammelsberg's Mineralchemie*, 540.)

Chlorite Slate.—This name is applied to chlorite occurring in mountain masses, including, however, those which are made up in like manner of ripidolite.

Chlorite-Spar. See Chloritoïde.

CHLORITES. $MClO^2$. (Millon, Ann. Ch. Pys. [3] vii. 298; Ann. Ch. Pharm. xlvi. 281.)—Salts of chlorous acid. Their general properties are described, together with those of the acid, at page 910. Only a few of them have been studied individually.

Chlorite of Barium. $BaClO^2$.—Obtained by saturating chlorous acid with baryta. By quickly evaporating the solution and finishing the evaporation in vacuo, it may be obtained crystallised and free from chlorite. It dissolves readily in water, and decomposes at 235° C.

Chlorite of Lead, $PbClO^2$, is prepared by adding nitrate of lead to chlorous acid nearly neutralised with lime or baryta, washing the sulphur-yellow scaly precipitate thereby produced, and drying it. If the solution be warmed before adding the nitrate of lead, the chlorite of lead is deposited in larger crystalline scales. The salt decomposes with a kind of explosion at 126° C. (Millon), at 100° (Schiel, Ann. Ch. Pharm. cix. 317). It sets fire to flowers of sulphur when triturated therewith (Millon); when rather large quantities of the salt are mixed with sulphur or a sulphide of an electronegative metal, the mixture takes fire spontaneously after some time (Schiel). Chlorite of lead introduced into sulphydric acid gas blackens at first, but afterwards turns white, from formation of sulphate of lead. With a mixture of equal parts of strong sulphuric acid and water, it evolves pure chlorous anhydride (Cl^2O^3), especially between 40° and 50° C., and yields 88·75 per cent. of sulphate of lead. (Millon.)

The mother-liquor filtered from the precipitate of chlorite of lead in the above-described mode of preparation, deposits on the sides of the vessels, small sparingly soluble yellowish crystals, which appear to be a compound of chlorite and chloride of lead. (Schiel.)

Chlorite of Potassium. $KClO^2$.—Potash-ley, mixed with excess of chlorous acid, forms a deep red liquid, which, when concentrated, gives off chlorous anhydride, and leaves neutral chlorite of potassium in the form of a very deliquescent salt. If, on the contrary, chlorous acid be gradually added to an excess of hydrate of potassium, the formation of the neutral salt takes a longer time, and even after the liquid has become colourless, the presence of free chlorous acid may be detected by its power of converting nitrate of lead into the peroxide. The saline solution must be quickly evaporated, otherwise the chlorite of potassium will be completely resolved into chloride and chlorate. The same decomposition takes place if it be heated to 160° C. (Millon.)

Chlorite of Silver. $AgClO^2$.—Prepared by mixing a soluble chlorite containing a slight excess of base with nitrate of silver, and boiling the resulting precipitate of chlorite and oxide of silver with water. The solution on cooling deposits the salt in yellow crystalline scales. At 105° C. it decomposes with explosion. A mixture of it with sulphur takes fire when triturated with a glass rod. In preparing the salt, an excess of chlorous acid must be avoided, as it would thereby be quickly resolved into chlorate and chloride. (Millon.)

Chlorite of Sodium. $NaClO^2$.—Deliquescent. Resembles the potassium-salt, but is not decomposed by a heat below 250° C. (Millon.)

Chlorite of Strontium. $SrClO^2$.—Deliquescent. Decomposes at 208° C. (Millon.)

CHLORITOÏDE. *Chlorite Spar, Barytophyllite, Masonite.*—A coarsely foliated massive silicate of alumina and iron found at Kosoibrod in the Ural, Bregratten in the Tyrol, and Gummuch-dagh in Asia Minor. Its specific gravity is 3·557; hardness 5·5 to 6; colour dark grey or greenish black; lustre faint and pearly. Gives off water when heated in a tube, is infusible before the blowpipe, but becomes darker and magnetic. It dissolves completely in sulphuric acid.

Allied to chloritoïde are: *Masonite*, from Rhode Island, which fuses with difficulty to a dark green enamel, and *Sismondine*, a dark greyish or blackish green mineral of specific gravity 3·565 and hardness 5·5. Nearly infusible before the blowpipe, occurring in the chlorite slate of St. Marcel.

Analysis: *Chloritoïde.*—1. O. Erdmann (J. pr. Chem. vi. 86).—2. Bonsdorff (Berz. Jahresber. xviii. 233).—3. Hermann (J. pr. Chem. liii. 13).—4. Smith (Ann. Min. [4] xviii. 300).—5. Kobell (J. pr. Chem. lviii. 40. *Masonite*, Whitney, (Proc. Boston Soc. Nat. Hist. 1849, p. 100). *Sismondine*, Delesse (Ann. Ch. Phys. [3] ix. 385).

Chloritoïde	SiO^2	Al^4O^3	Fe^4O^3	Fe^2O	Mn^2O	Mg^2O	Lime and alkali	H^2O
1. Kosoibrod .	24·90	46·20	—	28·89	—	—	—	— = 99·99
2. ,, .	27·48	35·57	—	27·05	0·30	4·29	—	6·95 = 101·64
3. ,, .	24·54	30·72	17·8	17·80	—	3·75	—	6·38 = 99·97
4. Gummuch-dagh	23·75	39·84	—	27·62	0·52	0·58	0·94	6·85 = 100·10
5. Bregratten .	26·19	38·30	6·00	21·11	—	3·30	—	5·50 = 100·40
Masonite .	28·27	32·16	—	33·72	—	0·13	—	5·00 = 99·28
Sismondine .	24·1	43·2	—	23·8	—	—	—	7·6 = 98·7

Among these analyses Nos. 3 and 5 of chloritoïde are the only ones in which the degree of oxidation of the iron appears to have been correctly determined; these agree approximately with the formula $(2M^2O.SiO^2).(M^4O^3.SiO^2) + 2aq.$, which, by substituting proto- for sesqui-equivalent metals, may be reduced to $M^2O.2(M^4SiO^4.aq)$. (*Rammelsberg's Mineralchemie*, p. 864; Dana, ii. 298.)

CHLOROBENZALDIDE. Syn. with Chloride of Benzoyl. (See Benzoyl, Chloride of, p. 566.)

CHLOROBENZAMIDE. See Benzamide (p. 540).

CHLOROBENZENE. See Benzene (p. 543).

CHLOROBENZIDE. Syn. with Trichlorobenzene. (See Benzene, p. 543).

CHLOROBENZIL. $C^{14}H^{11}ClO^2$. (Cahours, Ann. Ch. Phys. [3] xxiii. 350.) —Formed by the action of pentachloride of phosphorus on benzilic acid: the product is distilled, and the portion which comes over above 250° C. washed, dried, and rectified. It is a colourless, strongly-smelling oil, heavier than water; boils at about 270°. By exposure to moist air, or by the action of hot strong potash, it is quickly decomposed into chloride and benzilate. With ammonia and phenylamine, it yields crystalline products. F. T. C.

CHLOROBENZOIC ACID. See Benzoic Acid.

CHLOROBENZOL. Syn. with Chloride of Benzylene. (See Benzylene, Chloride of, p. 577.)

CHLOROBENZONITRILE. See Benzonitrile (p. 563).

CHLOROBENZOPHENIDE. See Benzoic Ethers under Benzoic Acid (p. 554).

CHLOROBENZOYL, CHLORIDE OF. See Benzoyl, Chloride of (p. 56).

CHLOROCAFFEINE. $C^8H^9ClN^4O^2$.—A product obtained by the incomplete action of chlorine on caffeine suspended in water (p. 708). When purified by three or four crystallisations from water, it forms a light bulky mass. From alcohol it crystallises in needles. By the continued action of chlorine, it is resolved into chloride of cyanogen, methylamine, and amalic acid. (Rochleder, Wien Akad. Ber. 1858 ii. 96.)

CHLOROCAMPHENE. See Camphene (p. 724).

CHLOROCARBO-HYPOSULPHURIC ACID. Syn. with Trichloromethylsulphurous Acid. (See Methyl.)

CHLOROCARBONIC ACID. Syn. with Oxychloride of Carbon, Chloride of Carbonyl, or Phosgene (p. 774).

CHLOROCARBONIC ETHERS. Compounds produced by the action of chloride of carbonyl on the alcohols. They may be regarded as compounds of carbonic anhydride with the chlorides of the alcohol-radicles, or as bodies formed on the mixed type HHO.HCl, in which 2 at. of hydrogen are replaced by carbonyl, CO, and the third by an alcohol-radicle, R:

$$CO^2.RCl = \left.\begin{matrix} CO'' \\ R \end{matrix}\right\} \begin{matrix} Cl \\ O \end{matrix}$$

Their formation is represented by the equation:

$$CO''\left\{\begin{matrix} Cl \\ Cl \end{matrix}\right. + \left.\begin{matrix} R \\ H \end{matrix}\right\} O = HCl + \left.\begin{matrix} CO'' \\ R \end{matrix}\right\} \begin{matrix} Cl \\ O \end{matrix}$$

Chlorocarbonate of Methyl. $C^2H^3ClO^2 = \left.\begin{matrix} (CO)'' \\ CH^3 \end{matrix}\right\} \begin{matrix} Cl \\ O \end{matrix}$. (Dumas and Péligot, Ann. Ch. Phys. lviii. 52.)—Obtained by introducing wood-spirit into a large flask filled with phosgene-gas:

$$CH^3.H.O + COCl^2 = HCl + C^2H^3ClO^2.$$

Colourless, very fluid oil, heavier and more volatile than water; has a penetrating odour; burns with a green flame. Gaseous ammonia converts it into carbamate of methyl (urethylane):

$$CO^2.CH^3Cl + NH^3 = \left.\begin{matrix} N.H^2(CO)'' \\ CH^3 \end{matrix}\right\} O + HCl.$$

Chlorocarbonate of Ethyl. $C^3H^5ClO^2$. (Dumas and Péligot, Ann. Ch. Phys. liv. 226.—Cloez, *ibid.* [3] xvii. 303.—Cahours, *ibid.* [3] xix. 346.)—Prepared like the preceding; also by the mutual action of alcohol and perchloroformic ether, or perchlorinated oxalate of methyl:

$$\underset{\substack{\text{Perchloro-}\\\text{formate of}\\\text{ethyl.}}}{C^3Cl^6O^2} + \underset{\text{Alcohol.}}{2C^2H^6O} = \underset{\substack{\text{Chlorocar-}\\\text{bonate of}\\\text{ethyl.}}}{C^3H^5ClO^2} + \underset{\substack{\text{Trichlorace-}\\\text{tate of}\\\text{ethyl.}}}{C^4H^5Cl^3O^2} + 2HCl.$$

$$\underset{\substack{\text{Perchlor-}\\\text{oxalate of}\\\text{methyl.}}}{C^4Cl^6O^4} + \underset{\text{Alcohol.}}{4C^2H^6O} = \underset{\substack{\text{Chlorocar-}\\\text{bonate of}\\\text{ethyl.}}}{2C^3H^5ClO^2} + \underset{\substack{\text{Oxalate of}\\\text{ethyl.}}}{C^6H^{10}O^4} + 4HCl.$$

Colourless liquid, very mobile, having a suffocating odour which irritates the eyes Perfectly neutral to test-paper. Specific gravity 1·139 at 15° C. Vapour-density 3·823. Boils at 94° C. Very inflammable. Burns with a green flame. Decomposed by hot water, not by cold. Ammonia converts it rapidly into chloride of ammonium and carbamate of ethyl.

Chlorocarbonate of Amyl, $C^6H^{11}ClO^2$, appears to be formed by the action of phosgene gas on amylic alcohol, but is immediately decomposed by moisture and converted into carbonate of amyl.

CHLOROCEROTIC ACID. See Cerotic Acid (p. 887).

CHLOROCINNAMIC ACID. See Cinnamic Acid.

CHLOROCINNOSE. Hydride of Tetrachlorocinnamyl. (See Cinnamyl.)

CHLOROCHLORIC ACID. Cl^6O^{13} (?) A compound obtained, according to Millon, (Ann. Ch. Phys. [3] vii. 298) by passing euchlorine (p. 913) through a series of U-tubes cooled by freezing mixtures, the first to 0° C., the others to −18°. Hydrochloric acid then condenses in the first, and chlorochloric acid in the rest, while free chlorine escapes at the end. Chlorochloric acid thus obtained, is a yellowish-red liquid, which boils at 32° C., and is converted into a yellow gas, which decomposes with explosion at 70°. With caustic potash, it yields a mixture of 2 at. chlorate and 1 at. chlorite of potassium, whence its composition is inferred:

$$Cl^6O^{13} + 3K^2O = 4KClO^3 + 2KClO^2.$$

Chlorochloric acid resembles perchloric oxide, ClO^2, in most of its properties, and approaches very nearly to it in composition ($6ClO^2 = Cl^6O^{12}$); indeed it is most probably nothing but perchloric oxide mixed with excess of chlorine (see p. 913.)

CHLOROCODEINE. See Codeine.

CHLOROCOMENIC ACID. See Comenic Acid.

CHLOROCUMENE. See Cumene.

CHLOROCUMINOL. See Cuminol.

CHLOROCYANAMIDE. } See Cyanamide.
CHLOROCYANILIDE. }

CHLORODRACONESIC ACID. Syn. with Chloranisic Acid. (See Anisic Acid.)

CHLORODRACONYL. When chlorine is passed into oil of tarragon, a viscid oily liquid is found, called *chloride of draconyl*, containing 39·9 per cent. C and 3·5 H, answering approximately to the formula $C^{10}H^{10}Cl^2O.Cl^2$; and this, when treated with alcoholic potash, yields another viscid oil, *chlorodraconyl*, containing 42·5 C and 3·4 H; possibly chloride of draconyl minus the elements of water. (Laurent, Rev. scient. x. 6.—Gerh. iii. 355.)

CHLORŒNANTHIC ACID. See Œnanthic Acid.

CHLOROFORM. *Dichlorinated chloride of methyl. Perchloride of formyl.* $CHCl^3$. Soubeiran, Ann. Ch. Phys. [2] xlviii. 131.—Soubeiran and Mialhé, Ann. Ch. Pharm. lxxi. 225.—Liebig, *ibid.* i. 198; Dumas, Ann. Ch. Phys. [2] lvi. 115.—Regnault, *ibid.* lxxi. 577.—Gm. vii. 342.)—Chloroform was discovered in 1831 by Soubeiran, who called it *Ether bichlorique*, and independently in 1832 by Liebig, who regarded it as a chloride of carbon: its true constitution was discovered by Dumas in 1834. Hutman (J. Chim. méd. [3] iv. 476) states, on the authority of Porta's *Magia naturalis* and Scott's *Letters on Demonology and Witchcraft*, that it was known in former times, and used as a means of producing insensibility.

Formation and Preparation.—1. Chloroform is produced, together with monochlorinated chloride of methyl, CH^2Cl^2, when a mixture of chlorine and gaseous chloride of methyl is exposed to the sun's rays. If the two gases be made to pass continuously into a vessel exposed to the sun and connected with a series of cooled receivers, the chloroform, being the least volatile of the products formed, condenses first, and if the current of chlorine be made rather strong, and the receivers not much cooled, the product consists almost wholly of chloroform.

2. By the action of alkalis on chloral:

$$\underset{\text{Chloral.}}{C^2HCl^3O} + KHO = \underset{\text{Chloroform.}}{CHCl^3} + \underset{\text{Formate of potassium.}}{CHKO^2}.$$

Chloral is distilled with excess of aqueous potash, soda or baryta, or with milk of lime, and the oily distillate is repeatedly agitated with water, separated from the water as completely as possible by decantation, and distilled with 6 or 8 times its volume of strong sulphuric acid in a perfectly dry apparatus. (Liebig.)

3. By the action of nascent hydrogen upon tetrachloride of carbon. (Geuther, p. 765.)

4. By boiling trichloracetic acid with aqueous alkalis:

$$C^2HCl^3O^2 + K^2O = CHCl^3 + K^2CO^3.$$

5. By the action of hypochlorites, or of chlorine, in presence of alkalis on various organic substances, viz.: *a.* On methylic, ethylic, and amylic alcohols, perhaps also on all alcohols of the series $C^nH^{2n+2}O$. With common alcohol and hypochlorite of calcium the principal reaction appears to be:

$$C^2H^6O + 5CaClO = CHCl^3 + Ca^2CO^3 + 2CaCl + CaHO + H^2O;$$

but other products are likewise formed, and chlorine is set free.—*b.* On acetic acid and acetates; probably thus:

$$C^2H^4O^2 + 3CaClO = CHCl^3 + Ca^2CO^3 + CaHO + H^2O.$$

c. On acetone.—*d.* On ethylsulphate or ethyltartrate of calcium.—*e.* On oil of turpentine and its isomers, the oils of lemon, bergamot, copaiba, &c.

The most economical method of preparing chloroform, and that which is always adopted on the manufacturing scale, is the distillation of alcohol with chloride of lime. The proportions used are about 6 pts. chloride of lime diffused through 30 pts. water, and 1 pt. alcohol of 33° Beaumé. The addition of slaked lime is also advantageous, as it absorbs the chlorine, which would otherwise be set free, and thereby diminishes the quantity of secondary products. The following mode of preparation on the large scale is given by Kessler (J. Pharm. [3] xiii. 162).

The apparatus consists of a large leaden cylinder, the sides of which are soldered with lead. Through the middle of the upper end passes a vertical rod, provided at the bottom with fans, and at the top with a curved handle, its lower extremity turning on a pivot in the base of the cylinder. By this arrangement, the mixture may be stirred up during the operation, and the heat thereby equally diffused. In the upper end of the cylinder there is also a wider aperture, which can be closed at pleasure, and through which the materials are introduced; through a third aperture is inserted the delivery-tube by which the chloroform vapour is conveyed to the condensing apparatus. Opposite to this tube there passes, through the upper base of the cylinder, a leaden tube, widened above like a funnel, and reaching just below the surface of the liquid. Into this funnel-tube, at some distance below the funnel, is inserted a steam-pipe, serving to convey steam from a boiler to the inside of the funnel-tube; and above the point of insertion of the steam-pipe, the funnel-tube is furnished with a cock, which, when open, allows the steam to pass upwards to the funnel-tube, and when shut directs it into the mixture in the cylinder. This cock serves to regulate the supply of vapour, and thereby regulates the heat. The chloroform vapour passes upwards through a worm-tube, enclosed in a condensing vessel, to a cooled Woulfe's apparatus, the last bottle but one of which is half filled with alcohol, and the last with cotton saturated with alcohol. A close-shutting wooden cask may be used instead of the leaden cylinder. 40 kilogrammes (88·8 lbs.) of the strongest chloride of lime are introduced into the cylinder by means of a four-cornered wooden funnel adapted to its widest aperture, and provided, near its lower extremity, with two horizontal rollers pressing against each other, as in a rolling-mill; these, when turned by their handles, serve to drive the chloride of lime quickly into the cylinder. 4 kilogrammes (8·8 lbs.) of slaked lime are next introduced in the same manner, and then a hectolitre of water (22 gallons) at a temperature of 80° to 90° C., is poured in. The apparatus is now thoroughly luted, and the contents are well mixed by turning the fans. 4 kilogrammes of commercial alcohol are then poured in, together with the residues of former operations. If the distillation of the chloroform does not immediately begin, steam is admitted from the boiler, and stopped as soon as the distillation is fairly set up. If the evolution of vapour becomes too rapid, cold water is poured in through the funnel-tube. When the reaction is complete, steam is again admitted into the cylinder, and the contents, which are now heated to 100°, frequently stirred. After 3 litres (5¼ pints) have been distilled off, the residue contains scarcely any chloroform or alcohol. The contents of the cylinder are discharged by an opening in the bottom, the liquid portion drawn off, and used in the next operation. The alcohol in the last two Woulfe's bottles likewise serves for the following preparations, and the process may be repeated three or four times in a day. 1 kilogramme of chloride of lime yields from 60 to 80 grammes of pure chloroform.

According to Simerling (Arch. Pharm. [2] liii. 23), the largest quantity of chloroform, in proportion to the alcohol used, is obtained from a mixture of 8 pts. chloride of lime, 1 pt. quicklime, 1 pt. alcohol, and 40 pts. water; the rectified chloroform thus produced, amounts to nearly one-third of the alcohol consumed (8 grm. chloroform from 25 grm. alcohol).

The use of acetone for the preparation of chloroform is not advantageous, because the price of it is high, and the product does not exceed one-third of the acetone used. This proportion was obtained by first distilling 30 grm. acetone with 150 grm. chloride of lime mixed with water, and rectifying the watery distillate with 40 grm. chloride of lime. Chloroform obtained from wood-spirit has an empyreumatic odour, and always blackens when agitated with sulphuric acid. The largest product was 6 grm. chloroform from 50 grm. wood-spirit.

For other methods see Ann. Ch. Pharm. xix. 210.—*Gmelin's Handbook*, vii. 344.

Chloroform may be contaminated with alcohol, ether, and empyreumatic oils. According to Soubeiran, pure chloroform sinks in a mixture of equal parts of oil of vitriol and water. According to Kessler, chloroform containing alcohol diminishes in volume on the application of this test. The presence of alcohol causes opalescence when the chloroform is mixed with water, whereas pure chloroform remains clear (Mialhé, J. Chim. méd. [3] iv. 279). Chloroform containing alcohol acquires a green colour when mixed with chromic acid or with sulphuric acid and acid chromate of potassium; pure chloroform produces no green colour (Cottell, J. Pharm. [3] xiii. 359). Chloroform prepared from wood-spirit is much less pure than that obtained from alcohol. The former is specifically lighter than the latter, has a repulsive empyreumatic odour, and produces unpleasant sensations when inhaled. It is contaminated with about 6 per cent. of an empyreumatic oil, containing chlorine, burning with a smoky flame, lighter than water, and boiling between 85° and 133° C. This oil cannot be completely separated by simple rectification, but is nearly, but not quite, destroyed by distillation with sulphuric acid. A similar oil, but in smaller quantity, is likewise obtained in the preparation of chloroform from alcohol; 20 kilogrammes of chloroform from alcohol yielded, when rectified over the water-bath, only 40 grm. of residue consisting of this oil; it is heavier than water, has an odour different from that of the oil obtained from wood-spirit, and its boiling point varies from 68° to 117° C. (Soubeiran and Mialhé). According to Gregory (Proc. Roy. Soc. Edinb. 1850, p. 391), impure chloroform may be recognised by the disagreeable odour which it leaves, after evaporation, on a cloth which has been moistened with it, and by the yellow or brown colour which it imparts to pure oil of vitriol when agitated therewith. Pure chloroform placed upon oil of vitriol produces a contact-surface convex downwards; impure chloroform gives a plane contact-surface. According to **Roussin** (J. Pharm. [3] xxxiv. 206), the purity of chloroform may be tested by means of *dinitrosulphide of iron*, $Fe^6H^2S^5N^4O^4$ (a salt obtained by the action of ferric chloride or sulphate on a mixture of sulphide of ammonium and nitrite of potassium). Pure chloroform shaken up with this salt, remains colourless; but if it contains alcohol, ether, or wood-spirit, it acquires a dark colour. To purify chloroform, **Gregory** agitates it and leaves it in contact with oil of vitriol till the latter is no longer coloured by it, then removes the chloroform, and places it in contact with a small quantity of peroxide of manganese, to free it from sulphurous acid. According to **Abraham** (Pharm. J. Trans. x. 24), chloroform thus purified quickly decomposes, and is afterwards found to contain hydrochloric acid and free chlorine. According to **Christison** (*ibid.* x. 253), chloroform keeps well after being once treated with oil of vitriol; but the continued action of that liquid (especially if contaminated with nitrous acid) exerts a decomposing action upon it.

Properties.—Pure chloroform is a transparent and colourless oil of specific gravity 1·491 at 17° C. (**Regnault**); 1·52523 at 0° (**Pierre**). It boils at 61° (**Regnault**); at 63·5° with the barometer at 772·52 mm. (**Pierre**). In contact with platinum-wire and with the barometer at 27″ 7‴, it boils in a dry vessel at 60·8°, but in contact with water, at 57·3° (**Liebig**). Its vapour-density is 4·199, according to Dumas; 4·230 according to Regnault. By calculation (2 vol.) it is $\frac{12 + 1 + 3 \times 35\cdot5}{2} \times 0\cdot0693 = 4\cdot141$. Chloroform remains liquid and transparent at −16° C. (**Pierre**), but may be solidified by the cold produced by its own evaporation; when it is thrown upon a double filter, the rapid evaporation at the edges causes the remaining portion to solidify in white tufts (**Soubeiran** and **Mialhé**). It has a very pleasant, penetrating odour, a sweet, fiery taste, and its vapour, when inhaled, produces a sweet taste on the palate. The inhalation of a small quantity of the vapour causes excitement similar to that produced by nitrous oxide; but a larger quantity produces insensibility to pain, in fact, a kind of coma: hence it is extensively used in surgical operations.* According to **Robin** (Compt. rend. xxx. 52) and **Augendre** (*ibid.* xxxi. 679), chloroform preserves meat from putrefaction (200 times its weight, according to Augendre).

Chloroform dissolves slightly in water, imparting its sweet taste to the liquid. It mixes in all proportions with alcohol, and is partially precipitated therefrom by water. It dissolves rapidly in ether. It is quite insoluble in sulphuric acid.

It dissolves *phosphorus*, *sulphur*, *iodine*, and *iodoform*, also many *organic bases* and their *salts*. The solubility of several organic bases in chloroform has been determined by **Michael Pettenkofer** (Jahresber. f. Chem. 1858, p. 363) and **A. Schlimpert** (*ibid.* 1859, p. 405), whose statements however differ widely, as the following table will show:

Quantities of Alkaloïds dissolved by 100 *pts. of Chloroform.*

	Pettenkofer.	Schlimpert.		Pettenkofer.	Schlimpert.
Morphine . . .	0·57	1·66	Veratrine . . .	58·49	11 6
acetate . .	—	1·66	Atropine . . .	51·69	33·0
Narcotine . . .	37·17	—	Strychnine . .	20·16	14·1
Quinine . . .	57·47	15·0	nitrate . .	—	6·6
sulphate . .	—	0	Caffeine . . .	—	11·1
hydrochlorate .	—	11·1	Brucine . . .	56·79	14·0
Cinchonine . .	4·31	2·5	Digitaline . . .	—	1·25
sulphate . .	—	3·0	Aconitine . . .	—	22·0
Quinidine (?) . .	—	25·3	Santonine . . .	—	23·0

Decompositions.—1. Chloroform decomposes when exposed to air and light, with formation of chlorine, hydrochloric acid, and other products; but when kept under water, it remains unaltered (**Marson**, Pharm. J. Trans. viii. 69).—2. At a red heat

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* "For the introduction of this valuable remedy we are indebted to Dr. Simpson; and although ether, benzole, and many other liquids can produce insensibility to pain, chloroform is of all the most powerful as well as the most manageable. Of course great care must be taken to insure its purity, for the oils which accompany it are very deleterious; and in administering it, one person should do nothing but watch the pulse and respiration of the patient and remove the chloroform if necessary. With due precaution, chloroform is very safe; and this precaution will prevent its being used in cases where its use is contra-indicated by the disease of the heart, or by marked tendency to apoplexy." (**Gregory**, *Handbook of Organic Chemistry*, 3rd ed. London, 1852, p. 178.)

its vapour appears to be resolved, partly into trichloride of carbon and hydrogen gas, partly into carbon, hydrochloric acid, and chlorine:

$$2CHCl^3 = C^2Cl^6 + H^2$$

and:

$$CHCl^3 = C + HCl + Cl^2$$

The liberation of chlorine in this manner is applied to the detection of chloroform in blood. A quantity of blood, not less than an ounce, is introduced, immediately after its separation from the organism, into a flask connected by a cork with a knee-shaped tube somewhat drawn out in the horizontal arm. A strip of paper, moistened with starch-paste and iodide of potassium, is inserted into the end of this tube; the drawn-out part is heated to redness; and the flask is heated in a water-bath. The vapour of chloroform thereby evolved is decomposed at the red-hot part of the tube, and the liberated chlorine turns the paper blue. This method is said to be capable of detecting 1 pt. of chloroform in 1,000,000 pts. of blood (Ragsky, J. pr. Chem. xlvi. 170). According to Duroy (J. Pharm. [3] xx. 401), it is not to be depended on unless the blood be taken from the animal immediately after the inhalation of the chloroform, or immediately after death. Duroy considers it better to pass a stream of cold air through the blood; then pass the air, together with the chloroform-vapour, through a red-hot tube, and thence into a solution of nitrate of silver, whereupon, if chloroform be present, a precipitate of chloride of silver will be formed.

3. Chloroform cannot be set on fire in the air, not even with the aid of a wick; but its vapour passed into the flame of a spirit-lamp, burns with smoke; a mixture of chloroform and alcohol in equal measures, burns with a very smoky flame and pungent odour, producing hydrochloric acid (Soubeiran, Liebig). It imparts a green colour to the flame of a candle (Liebig).—4. Chloroform repeatedly distilled in a stream of dry *chlorine*, is resolved into HCl and C^2Cl^4 (Regnault).—5. Chloroform heated with *nitric acid* evolves but a small quantity of nitrous fumes (Soubeiran).—6. When kept under *sulphuric acid*, it gradually gives off vapours of hydrochloric acid. The alcoholic solution of chloroform, mixed with *nitrate of silver*, does not deposit any chloride of silver, even in the course of a month (Soubeiran).—7. Boiled with *potash-ley* in a closed tube, it is resolved into formate and chloride of potassium; but the decomposition is imperfect (Dumas):

$$CHCl^3 + 2K^2O = CHKO^2 + 3KCl.$$

Chloroform is not decomposed by boiling with aqueous alkalis in an open vessel (Liebig). Alcoholic potash boiled for a long time with chloroform, produces formate of potassium (Regnault). A mixture of chloroform, potash, and alcohol, heated in a sealed tube to 100° C. for a week, yields ethylene-gas and formic acid (Berthelot, Ann. Ch. Phys. [3] liv. 87).—8. Chloroform vapour passed over *ignited baryta* or *lime*, yields metallic chloride, carbonate, and charcoal; if the heat be moderate, these products are not accompanied by any gas; but at a full red heat, carbonic oxide is produced by the action of the charcoal on the alkaline carbonate (Liebig, Soubeiran).—9. Chloroform may be distilled over *potassium* without decomposition; but potassium heated in its vapour takes fire with explosion, forming chloride of potassium mixed with charcoal (Liebig). It is not decomposed by *sodium*, even when heated with it to 200° C. in a sealed tube (Heintz). Chloroform is not decomposed by heating with cyanide of potassium, mercury, or silver, even on the addition of alcohol. (Bouchardat.)

A mixture of chloroform and ammonia-gas is decomposed by a heat approaching to dull redness, yielding chloride and cyanide of ammonium:

$$CHCl^3 + 5NH^3 = 3NH^4Cl + NH^4.CN.$$

If the temperature be raised too high, a brown substance is formed, probably paracyanogen. When a solution of ammonia in absolute alcohol is heated with chloroform to a temperature between 180° and 190° C., formate of ammonium may be produced as well as cyanide; in many instances also neither of these salts is formed, but only a brown mass, probably consisting for the most part of paracyanogen. (Heintz, Pogg. Ann. xcviii. 263.)

Chloroform and *phenylamine* do not react at ordinary temperatures; but when equal volumes of the two are heated to 180°—190° C. in a sealed tube, hydrochlorate of phenylamine is formed, together with hydrochlorate of formyl-diphenyl-diamine.

$$CHCl^3 + 4(N.H^2.C^6H^5) = 2[(N.H^2.C^6H^5).HCl] + [N^2.H.(CH)'''(C^6H^5)^2].HCl.$$

(Hofmann, Proc. Roy. Soc. ix. 229.)

CHLOROFORMYL-HYPOSULPHURIC ACID. Syn. with DICHLOROMETHYL-SULPHUROUS ACID. (See METHYL.)

CHLOROGENIC ACID. Syn. with CAFFETANNIC ACID (p. 709).

CHLOROGENIN. A substance which accompanies rubian precipitated from extract of madder by sub-acetate of lead, and forms a green powder when boiled with sulphuric or hydrochloric acid.

CHLOROMELAL. A product of the action of chlorine on hydrate of myricyl (*q. v.*) Its analysis agrees approximately with the empirical formula $C^{30}H^{45\cdot5}Cl^{14\cdot5}O$ (Brodie, Ann. Ch. Pharm. lxxi. 144.)

CHLOROMELANE. See CRONSTEDTITE.

CHLOROMELANILINE. See MELANILINE.

CHLOROMERCURATES. Compounds of mercuric chloride with basic metallic chlorides, or with hydrochlorates of organic bases, *e. g. Chloromercurates of potassium*, KCl.HgCl; KCl.2HgCl; KCl.4HgCl; *Chloromercurate of morphine*, $C^{17}H^{19}NO^3.HCl.4HgCl$. They are obtained by mixing the aqueous or alcoholic solutions of the component salts, and are for the most part crystallisable.

CHLOROMESITATE OF METHYLENE. $C^8H^{10}Cl^2O^2$. — A crystalline substance produced by the action of chlorine on methylic alcohol (*q. v.*)

CHLOROMETHYLASE. $C^2H^2Cl^2$. — An oily liquid produced by the action of potash on acetate of trichloromethyl. It has the composition of *dichlorethylene*, (Laurent, Ann. Ch. Phys. lxiii. 382.) (See ACETATE OF METHYL, p. 23.)

CHLORONAPHTHANE. See NAPHTHALENE.

CHLORONAPHTHALIC ACID. See NAPHTHALENE, CHLORINE-DERIVATIVES OF.

CHLORONICEIC ACID. This name was given by St. Evre (Ann. Ch. Phys. [3] xxv. 484), to an acid crystallising in microscopic four-sided needles, which he obtained by passing chlorine into a solution of benzoate of potassium, containing excess of potash. St. Evre assigned to this acid the formula $C^6H^5ClO^2$. But from the experiments of Pisani, made in Gerhardt's laboratory, it appears that this acid is nothing but chlorobenzoic acid, $C^7H^5ClO^2$. The acid prepared as above was found, after purification by repeated crystallisation, to be identical in composition and properties with chlorobenzoic acid prepared by the action of pentachloride of phosphorus on salicylic acid, or on salycilate of methyl. E. Kopp likewise obtained nothing but chlorobenzoic acid, by passing chlorine into a solution of benzoic acid in caustic soda. Hence also, it may be inferred that St. Evre's *chloroniceamide* is identical with chlorobenzamide; that *chloronicene*, a volatile liquid obtained by distilling chloroniceic acid with baryta or lime, is the same as chlorobenzene, C^6H^5Cl; and that *chloronicine*, a base obtained by the action of sulphide of ammonium on chloronicine, is identical with chlorophenylamine. (Gerh. iii. 980.)

CHLOROPAL. A hydrated ferric silicate, of which there are two varieties, the conchoïdal and the earthy. The former has a pistachio-green colour, is translucent on the edges, has a flat conchoïdal fracture; specific gravity 2·158; hardness 4·5. The latter has a light green colour, verging towards olive-green and brown, is sometimes compact, sometimes friable: the compact variety is very soft. The composition of this mineral varies considerably, as the following analyses will show: 1, 2, from Hungary (Bernhardi and Brandes, Schw. J. xxxv. 29); 3, 4, from the Meenser Steinberg, near Göttingen (Hiller, Jahresber. d. Chem. 1857, p. 671):

	SiO^2	Fe^4O^3	Al^4O^3	Mg^2O	Mn^2O	H^2O	
1. Conchoïdal	46	33	1	2	—	18	= 100
2. Earthy .	45	32	0·75	2	—	20	= 99·75
3. „ .	71·6	16·3	2·1	1·5	trace	8·3	= 99·8
4. Conchoïdal	39·7	28·0	3·7	2·4	trace	26·1	= 99·9

It is perhaps a mixture in variable proportions of opal with a hydrated ferric silicate, $Fe^4O^3.3SiO^2 + 3H^2O$, or $fe^2SiO^3 + H^2O$, or $(fe^2H^2)SiO^4$, the conchoïdal variety analysed by Hiller, containing about 41 per cent. of the ferric silicate, the earthy variety, 70 per cent. (Jahresber. *loc. cit.*)

CHLOROPALLADATES. Compounds of dichloride of palladium with the more basic metallic chlorides, or with hydrochlorates. They are not much known.

CHLOROPALLADITES. Compounds of protochloride of palladium with the more basic metallic chlorides, or with hydrochlorates of organic bases; *e. g.* chloropalladite of potassium, KCl.PdCl; chloropalladite of strychnine, $C^{21}H^{22}N^2O^2.HCl.PdCl$.

CHLOROPALMITIC ACID. See PALMITIC ACID.

CHLOROPERCHLORIC ACID. Cl^6O^{17}?— A compound said to be produced by exposing chlorous anhydride to sunshine, the containing vessel being at the same time immersed in water of 20° C. It is a reddish brown liquid which is decomposed by heat, but not explosively; forms extremely dense white fumes in contact with moist air, and is decomposed by potash; yields 1 at. chlorite and 2 at. chlorate of potassium: $Cl^6O^{17} + 3K^2O = 2KClO^2 + 4KClO^4$. (Millon, Ann. Ch. Phys. [3] vii. 298. It is perhaps hyperchloric oxide, $Cl^6O^{18} = 3Cl^2O^6$ (p. 907).

CHLOROPHÆITE. A ferrous silicate, occurring in foliated or granular massive forms, in the Faroe Islands, also in the neighbourhood of Fife and of Newcastle. It has a dark green colour, and subresinous lustre; specific gravity 2·02; hardness 1·5 to 2. According to Forchhammer's analysis (Berz. Jahresber. xxiii. 265), it contains 32·85 per cent. silica, 21·56 protoxide of iron, 3·44 magnesia, and 12·15 water, whence the formula $2(\frac{7}{9}Fe^2O.\frac{2}{9}Mg^2O).3SiO^2 + 12H^2O$, which may be represented as an orthosilicate of the form $(M^4H^8)Si^3O^{12} + 8H^2O$.

CHLOROPHÆNERITE. A hydrated ferrous silicate, found in cavities of the amygdaloïdal porphyry of Weissig in Saxony. It is blackish-green, with dirty apple-green streak; not very hard; of specific gravity 2·684. Analysis gave 59·4 per cent. SiO^2, 12·3 Fe^2O, and 5·7 H^2O, besides alumina, magnesia, lime, potash, and soda. (Jenzsch, Chem. Centr. 1856, 76.)

CHLOROPHANE. A variety of fluorspar, which emits a green light on calcination.

CHLOROPHENESIC ACID. Syn. with Dichlorophenic acid, $C^6H^4Cl^2O$. (See Phenic Acid.)

CHLOROPHENISIC ACID. Syn. with Trichlorophenic Acid.

CHLOROPHENUSIC ACID. Syn. with Pentachlorophenic Acid.

CHLOROPHENYL. This name was applied by Laurent to a crystalline substance obtained by the action of boiling nitric acid on trichlorophenic acid. It crystallised in yellow scales insoluble in water, soluble in alcohol and ether, and subliming in very brilliant scales. Analysis gave 37·8 per cent. C, 1·88 H, and 54·30 Cl. (Gerh. ii. 28.)

CHLOROPHOSPHIDE OF NITROGEN. See Nitrogen.

CHLOROPHYLL. (Berzelius, Ann. Ch. Pharm. xxi. 257, 262; xxvii. 296.—Verdeil, Compt. rend. xxiii. 689.—Schulze, *ibid.* xxxiv. 683.—Mulder, Ann. Ch. Pharm. lii. 421.)—The colouring matter of leaves and the other green parts of plants. It is extracted by digesting green leaves for several days with ether, evaporating the filtered liquid to dryness, treating the residue with boiling alcohol, and adding to the solution a small quantity of milk of lime, which precipitates all the colouring matter, while the alcohol retains a quantity of fat which was mixed with it. The chlorophyll is separated from the lime by means of hydrochloric acid and ether, which dissolves the colouring matter, forming a green stratum at the top of the liquid. By evaporating the ether, the chlorophyll is obtained in the pure state.

Chlorophyll thus prepared is an earthy powder, of a deep green colour, unalterable in the air, infusible, sustaining a heat of 200° C. without decomposition, but decomposing at higher temperatures. It is insoluble in water, even at the boiling heat; easily soluble in alcohol, less in ether. Acids and alkalis dissolve it with green colour: a solution of alum precipitates it. Nascent hydrogen decolorises it like indigo (Mulder). Mulder represents chlorophyll by the formula $C^9H^9NO^4$, which however cannot be considered as established. According to Verdeil, chlorophyll has a great analogy to the colouring matter of blood, and like that substance, contains a large quantity of iron. According to Morot (Jahresber. f. Chem. 1859, p. 562), chlorophyll is $C^{18}H^{20}N^2O^3$, and is always accompanied by a fatty substance, $C^8H^{14}O$. The latter is produced by the action of atmospheric oxygen on starch, according to the equation;

$$2C^6H^{10}O^5 + O^2 = C^8H^{14}O + 4CO^2 + 3H^2O.$$

and chlorophyll results from the simultaneous action of carbonic acid and ammonia on this fat, under the influence of light:

$$C^8H^{14}O + 2NH^3 + 10CO^2 = C^{18}H^{20}N^2O^3 + O^{18}.$$

According to Schultze, chlorophyll forms the colouring matter of several green animalcules inhabiting ponds and ditches, such as polypes, turbellarias, and infusoria (*Hydra viridis*, *Vortex viridis*, *Mesostomum viridatum*, *Derostomum cæcum*, *Stentor polymorphus*, *Ophrydium versatile*, *Bursaria vernalis*).

The name *Erythrophyll* has been given to the red colouring matter of leaves in autumn. It is soluble in water and alcohol; dissolves with brown colour in alkalis, and forms with lead-salts, a precipitate of a fine green colour.

CHLOROPHYLLITE. An altered form of cordierite, found at Haddam in Connecticut, and Unity, New Hampshire. It occurs in trimetric crystals of the same form as the original cordierite, of greyish or brownish-green colour, and pearly lustre; specific gravity 2·782. According to Rammelsberg's analysis, it contains 46·31 per cent. SiO^2, 25·17 Al^4O^3, 10·99 Fe^4O^3, 10·91 Mg^2O, trace of Mn^2O, 0·58 Ca^2O, and 6·70 water (= 100·66), which numbers, if a small quantity of the iron be supposed to exist as protoxide, may be nearly represented by the formula $2(M^2O.M^4O^3.2SiO^2) + 3aq.$, or

$2(M^2m^6)Si^2O^8 + 3aq.$, which is that of a hydrated cordierite. (*Rammelsberg's Mineralchemie*, p. 833.)

CHLOROPICRIN. CCl^3NO^2. (Stenhouse, Phil. Mag. [3] xxxiii. 53.—Gerhardt and Cahours, Compt. chim. 1849, pp. 34 and 170.)—This compound may be regarded as marsh-gas, CH^4, in which 1 at. H is replaced by NO^2, and 3 more by chlorine. It is produced: 1. By the distillation of picric acid, styphnic acid, or chrysammic acid with chloride of lime and water: hence also when the bodies which yield either of these three acids by treatment with nitric acid are first boiled with nitric acid and then distilled with chloride of lime. To these belong: creosote, salicin, indigo, cumarin, the yellow resin of Botany Bey, liquid storax, benzoin, Peru-balsam, galbanum, gum assafœtida, ammoniacum, purree, aloes, extract of Campeachy wood, log-wood, fustic, red sandal-wood, &c. Lastly, Dammara resin, and the chlorinated resin formed in the decomposition of usnic acid by chlorine, likewise yield chloropicrin, when treated with nitric acid and chloride of lime.—2. By treating picric acid with chlorine water or aqua-regia, or a mixture of chlorate of potassium and hydrochloric acid.

To prepare it, aqueous picric acid is distilled with chloride of lime till, after about a quarter of an hour's boiling, no more heavy oil passes over with the water. Should the residue be still yellow, it must be redistilled with fresh chloride of lime. The oil is separated from the watery distillate, washed with water to which a little carbonate of magnesium has been added, dried by placing it over chloride of calcium, and rectified.

Chloropicrin is a transparent, colourless, strongly refracting oil, of specific gravity 1·6657, boiling at 120° C. Its odour, in the dilute state, is peculiarly aromatic, but in the concentrated state very sharp, and attacks the nose and eyes less persistently, but quite as violently, as volatile chloride of cyanogen and oil of mustard. It is neutral to vegetable colours. It dissolves sparingly in water, very easily in alcohol and ether.

Chloropicrin sustains without alteration a heat of 150° C.; but when passed through a red-hot tube, it is completely decomposed, yielding nitric oxide, chlorine, and trichloride of carbon. A small piece of potassium gently heated in the oil, causes strong explosion: at ordinary temperatures, it forms in a few days chloride and nitrate of potassium. Chloropicrin is not decomposed by aqueous potash, even after prolonged contact; but alcoholic potash gradually decomposes it, forming chloride and nitrate of potassium. Aqueous ammonia exerts scarcely any action upon chloropicrin; but with ammoniacal gas or alcoholic ammonia, it forms chloride and nitrate of ammonium. It is not acted upon by sulphuric, nitric, or hydrochloric acid, even at the boiling heat.

BROMOPICRIN. CBr^3NO^2. (Stenhouse, Phil. Mag. [4] viii. 36.)—Obtained, like chloropicrin, by distilling picric acid with solution of hypobromite of calcium (lime-water containing bromine), and purified by washing with carbonate of sodium, agitation with mercury, and digestion (not distillation) with chloride of calcium. It is a colourless liquid, heavier than water, having the acrid odour of chloropicrin. It is insoluble in water, easily soluble in alcohol and ether. It may be heated to its boiling point (above 100° C.) without decomposition, but is then decomposed, with evolution of brown-red vapours, even in an atmosphere of carbonic anhydride. At a higher temperature, it decomposes with slight explosion. The alcoholic solution is slowly precipitated by nitrate of silver in the cold, immediately when heated.

CHLOROPLATINATES. Compounds of dichloride of platinum with the more basic metallic chlorides, or with the hydrochlorates of organic bases: *e.g. Chloroplatinate of ammonium*, $NH^4Cl.PtCl^2$; *Chloroplatinate of Strychnine*, $C^{21}H^{22}N^2O^2.HCl.PtCl^2$. (See PLATINUM.)

CHLOROPLATINITES. Compounds of protochloride of platinum with more basic metallic chlorides: *Chloroplatinite of potassium*, KCl.PtCl. (See PLATINUM.)

CHLORORHODATES. Compounds of sesquichloride of rhodium with more basic chlorides, *e. g. Chlororhodate of ammonium*, $2NH^4Cl.R^2Cl^3$.

CHLORORUBIN. See RUBIAN and MADDER.

CHLOROSALICIN. See SALICIN.

CHLOROSALIGENIN. See SALIGENIN.

CHLOROSAMIDE. Syn. with HYDRIDE OF CHLORAZOSALICYL. (See SALICYL.)

CHLOROSPINEL. A grass-green spinel from Slatoust in the Ural, of specific gravity 3·591—3·594. It contains, according to two analyses by H. Rose (Pogg. Ann. i. 620):

Al^4O^3	Fe^4O^3	Mg^2O	Cu^2O	Ca^2O	
64·13	8·70	26·77	0·27	0·27	= 100·24
57·34	14·77	27·49	0·62	—	= 100·22

whence the formula $Mg^2O.(Al^4O^3 ; Fe^4O^3)$ or $Mg(Al ; Fe)^2O^2$. It is distinguished from Ceylonite (p. 843) by the absence of ferrous oxide.

CHLOROSTRYCHNINE. See Strychnine.

CHLOROSTYRACIN. See Styracin.

CHLOROSUCCIC ACID. An acid obtained by the metamorphosis of perchlorinated succinate of ethyl. (See Succinic Ethers.)

CHLOROSUCCINIMIDE. See Succinimide.

CHLOROTEREBENE. See Terebene.

CHLOROSULPHURIC ACID. See Sulphuryl, Chloride of.

CHLOROVALERISIC ACID. Syn. with Trichlorovaleric Acid. (See Valeric Acid.)

CHLOROVALEROSIC ACID. Syn. with Tetrachlorovaleric Acid.

CHLOROXALOVINIC ACID. See Oxalic Ethers.

CHLOROXAMETHANE. Syn. with Pentachlorinated Oxamate of Ethyl. (See Oxamic Ethers.)

CHLOROXETHIDE. Syn. with Chloroxalovinic Anhydride. (See Oxalic Ethers.)

CHLOROXETHOSE. C^4Cl^6O. (Malaguti, Ann. Ch. Phys. [3] xvi. 19.—Obtained by the action of monosulphide of potassium on perchloric ether:

$$C^4Cl^{10}O + 2K^2S = 4KCl + S^2 + C^4Cl^6O.$$

To prepare it, 50 pts. of monosulphide of potassium are heated with 16 pts. of perchloric ether and 200 pts. of alcohol of 95 per cent. Chloride of potassium is then deposited; the liquid assumes a dark colour; and after a day, the deposit of chloride of potassium becomes covered with crystals of sulphur. On adding water to the liquid, chloroxethose separates in the form of an oil.

It is a colourless, limpid, oily liquid, having an agreeable odour like that of meadow-sweet, and a saccharine taste. Specific gravity 1·654 at 20° C. Boils at 210° C. with slight decomposition. Insoluble in water, soluble in alcohol and ether. It is altered after some time by exposure to the air. It is not attacked by alkalis or by ordinary nitric acid; but nitric acid of specific gravity 1·5 attacks it strongly when heated. On exposing it to sunshine in an atmosphere of chlorine, crystals of perchloric ether make their appearance after a few days: $C^4Cl^6O + Cl^4 = C^4Cl^{10}O$. It likewise absorbs bromine in sunshine, producing perchlorobromic ether. Exposed to the action of chlorine under a layer of water, it yields hydrochloric and trichloracetic acids:

$$C^4Cl^6O + Cl^4 + 3H^2O = 4HCl + 2C^2HCl^3O^2.$$

CHLOROXYNAPHTHALIC ACID. See Oxynaphthalic Acid.

CHOCHOCA. A name applied by the natives of South America to dried potatoes prepared by exposing the peeled and boiled tubers to the alternate action of frost and sunshine.

CHODNEFFITE. Syn. with Cryolite.

CHOLACROL. $C^8H^{10}N^4O^{13} = C^8H^{10}(NO^2)^4O^5$ (?)—A product of the action of nitric acid upon bile. This action gives rise to both fixed and volatile products. The volatile substances formed are capric, caprylic, valeric, and butyric acid, together with an oily body which, when treated with strong caustic potash, is resolved into nitrocholic acid and cholacrol, which latter may be separated from the saline solution by decantation. It is an oily neutral body having a strong odour; dissolves sparingly in water, freely in alcohol and ether; when heated, it decomposes with slight explosion. (Redtenbacher, Ann. Ch. Pharm. lvii. 145.)

CHOLALIC ACID. $C^{24}H^{40}O^5$.—Syn. with cholic acid, the non-azotised acid obtained by the action of alkalis on taurocholic and glycocholic acids. (See Cholic Acid.)

CHOLEIC ACID. Syn. with Taurocholic Acid, the sulphuretted acid of bile.

CHOLESTERIC ACID. $C^8H^{10}O^5$.—This acid is produced, together with choloïdanic acid, oxalic acid, several volatile acids, and a resinous substance, by the action of nitric acid on cholesterin. Choloïdic and glycocholic acids treated with nitric acid yield the same products. To prepare it, cholesterin is treated with nitric acid in a retort, the distilled liquid being frequently poured back, whereby a resinous mass is produced, which slowly dissolves after prolonged boiling with excess of nitric acid. The liquid, when sufficiently concentrated in the retort, leaves an acid gummy residue, containing a large quantity of cholesteric acid, mixed with choloïdanic acid and a resinous substance; and this residue, on cooling, separates into two layers, the upper of which consists of crystalline choloïdanic acid, while the lower, which is viscid, consists chiefly of cholesteric acid containing a little oxalic acid. On saturating this liquid with ammonia, precipitating by nitrate of silver, and boiling the precipitate with water, cholesterate of silver is deposited in crystalline crusts, which, when decomposed by sulphuretted hydrogen, yield the acid.

Cholesteric acid is a yellowish gummy solid, resembling the gum of the cherry-tree. It is deliquescent; very soluble in water and alcohol; has an acid, bitter, and astringent taste, and is decomposed by distillation, giving off bitter vapours and leaving a considerable quantity of charcoal.

The formula of the *cholesterates* is $C^8H^8M^2O^5$. The alkaline and earthy salts are soluble and uncrystallisable; the cholesterates of the heavy metals are insoluble.

CHOLESTERIN. $C^{26}H^{44}O$.—This substance was first obtained by Conradi, in 1775, from human gall-stones, of which it sometimes constitutes nearly the entire substance. It has been found in human bile by Chevreul (Ann. Chim. xcv. 5; xcvi. 166); in the blood by Lecanu (Ann. Ch. Phys. lxvii. 54), Boudet (*ibid.* lii. 336), Denis (J. Chim. méd. [2] iv. 161), and by Becquerel and Bodier (Gaz. méd. No. xlvii.); in the brain (Couerbe, Ann. Ch. Phys. lvi. 281; Frémy, *ibid.* [3] ii. 486), in yolk of egg (Lecanu, J. Pharm. xv. 1; Gobley, *ibid.* [3] xii. 12), and in certain morbid products of the animal economy, such as cerebral concretions, scirrhous matter of the mesocolon, hydropic liquid of the abdomen, ovaries, testicles, &c. (Lassaigne Ann. Ch. Phys. ix. 324; O. Henry, J. Chim. méd. i. 280; Caventou, J. Pharm. xi. 462; Lehmann, Lehrb. d. Physiol. Chem. 2te Aufl. i. 286). The first exact analysis of cholesterin was made by Chevreul, who assigned to it the formula above given. Its metamorphoses have been studied by Marchand (J. pr. Chem. xvi. 37), Redtenbacher (Ann. Ch. Pharm. lvii. 145), Meissner and Schwendler (*ibid.* lix. 107; and J. pr. Chem. xxxix. 247), Zwenger (Ann .Ch. Pharm. lxvi. 5; lxix. 347), Heintz (Pogg. Ann. lxxix. 524), and Berthelot (Ann. Ch. Phys. [3] lvi. 51).

Cholesterin is easily prepared by crystallising *biliary calculi* from boiling alcohol, to which a little potash is added to dissolve any fatty acids that may be present. The cholesterin is then deposited in colourless nacreous laminæ. To obtain cholesterin from brain, that substance is treated with ether, the ethereal extract boiled with alcoholic potash, and the liquid left to cool. It then deposits cholesterin mixed with cerebrate and phosphate of potassium, from which the cholesterin may be dissolved out by ether.

Cholesterin is white, tasteless, inodorous, insoluble in water, sparingly soluble in cold alcohol, but dissolves very easily in boiling alcohol, from which it separates on cooling in beautiful crystalline nacreous laminæ, soft to the touch, and melting at 137° C. It dissolves also in ether, wood-spirit, oil of turpentine, soap-water, and neutral fats. A solution of cholesterin in a mixture of 2 vols. alcohol and 1 vol. ether deposits by spontaneous evaporation laminated transparent crystals of hydrate of cholesterin, $C^{26}H^{44}O + H^2O$, which give off their water at 100° C.

Cholesterin resists the action of concentrated alkaline solutions even at the boiling heat; but lime decomposes it at about 250° C., hydrogen being given off and the cholesterin being converted into an amorphous fatty body nearly insoluble in alcohol.

Cholesterin is attacked by *chlorine* and *bromine*, yielding substitution-products; the *chlorine* compound is $C^{26}H^{36}Cl^8O$. For the action of nitric acid upon cholesterin, see CHOLESTERIC ACID.

Cholesterin sublimes without alteration at 200° C., but decomposes at a higher temperature, yielding several oily products and a solid body. When distilled in a retort, it yields a carbonaceous residue and a neutral oily liquid insoluble in potash, from which a second distillation with water separates a volatile oil having the agreeable odour of geraniums.

When *strong sulphuric acid* is gradually added to a slightly heated mixture of cholesterin and dilute sulphuric acid, the cholesterin becomes soft, acquires a deep red colour, and decomposes, giving off all its oxygen in the form of water, and is changed, without evolution of gas, into three isomeric hydrocarbons, which Zwenger designates as cholesterilin, *a*, *b*, and *c*; they are insoluble in water, and may be freed from sulphuric acid by washing with that liquid. These hydrocarbons are easily crystallisable, and like cholesterin are remarkable for possessing high melting points. *a* has an earthy aspect, melts at 240° C., and is nearly insoluble in alcohol, very sparingly soluble in ether; *b* forms shining scales melting at 255°, moderately soluble in hot ether; if kept in the fused state it loses the power of crystallising; *c* is resinous without appearance of crystallisation, and melts at 127°, it is also soluble in hot ether.

With concentrated *phosphoric acid*, cholesterin forms two compounds, called cholesterone, *α* and *β*, isomeric with each other, but differing in physical properties. Cholesterone *α* forms very brilliant rectangular prisms, melting at 68° C., and distilling almost without alteration; easily soluble in alcohol and ether. The modification *β* forms small silky needles sparingly soluble in ether, nearly insoluble in alcohol.

The composition of cholesterilin and cholesterone agrees nearly with the formula

$C^{26}H^{42}$; they are, therefore, either isomeric or polymeric. Their formation from cholesterin is represented by the equation:

$$C^{26}H^{44}O - H^2O = C^{26}H^{42}.$$

This decomposition shows that cholesterin partakes of the nature of an alcohol; it is, in fact, homologous with cinnamic alcohol, and its formula may be written $C^{26}H^{43}.H.O$. Heated with acetic, butyric, benzoic, and stearic acids, it forms compound ethers, with elimination of water; thus with stearic acid:

$$\underset{\text{Stearic acid.}}{\left.\begin{matrix}C^{18}H^{35}O\\H\end{matrix}\right\}O} + \underset{\text{Cholesterin.}}{\left.\begin{matrix}C^{26}H^{43}\\H\end{matrix}\right\}O} = \underset{\text{Stearate of cholesteryl.}}{\left.\begin{matrix}C^{18}H^{35}O\\C^{26}H^{43}\end{matrix}\right\}O} + H^2O.$$

These ethers are prepared in the same manner as the glycerides, and are purified by boiling the product with eight or ten times its volume of alcohol, which extracts the unaltered cholesterin, and crystallising from boiling ether.

Benzoate of Cholesteryl, $C^{33}H^{48}O^2 = C^7H^5O.C^{26}H^{43}.O$, crystallises in small shining micaceous laminæ, which melt between 125° and 130° C., dissolve with moderate facility in ether, very sparingly in boiling alcohol. The *butyrate*, $C^4H^7O.C^{26}H^{43}.O$, is easily fusible, somewhat soluble in hot alcohol. The *stearate*, $C^{18}H^{35}O.C^{26}H^{43}.O$, crystallises in small shining needles, having a neutral reaction, sparingly soluble in cold ether, nearly insoluble in alcohol even at the boiling heat. The *acetate* has likewise been formed, but is difficult to purify, being more soluble in alcohol than the preceding compounds. (Berthelot.)

CHOLESTROPHANE. $C^5H^6N^2O^3$.—The name given by Rochleder to the final product of the action of chlorine on caffeine (*q. v.*), called also *nitrotheine* by Stenhouse, and regarded by Gerhardt as *dimethylparabanic acid*, $C^3(CH^3)^2N^2O^3$. It is also obtained by the action of nitric acid upon caffeine. It is soluble in alcohol, and crystallises in iridescent scales, which sublime at 100° C. Boiled with potash it yields carbonate and oxalate of potassium, and gives off ammonia (according to Rochleder), or rather methylamine.

CHOLIC ACID. *Cholalic Acid.** $C^{24}H^{40}O^5$.—This acid was discovered by Demarçay in 1838 (Ann. Ch. Phys. [2] lxvii. 177), further examined by Theyer and Schlosser (Ann. Ch. Pharm. xlviii. 77; l. 235), and finally by Strecker (*ibid.* lxv. 9; lxvii. 1; lxx. 161, 166). It is produced by the action of alkalis on the acids of bile, viz. glycocholic and taurocholic acids, the decomposition taking place in the manner represented by the equations:

$$\underset{\text{Glycocholic acid.}}{C^{26}H^{43}NO^6} + H^2O = \underset{\text{Cholic acid.}}{C^{24}H^{40}O^5} + \underset{\text{Glycocine.}}{C^2H^5NO^2}.$$

$$\underset{\text{Taurochloric acid.}}{C^{26}H^{45}NSO^7} + H^2O = \underset{\text{Cholic acid.}}{C^{24}H^{40}O^5} + \underset{\text{Taurine.}}{C^2H^7NSO^3}.$$

Cholic acid does not exist ready formed in normal bile, but is produced from the nitrogenised acids of bile during the putrefaction of that liquid after its removal from the body. Similar changes appear also to take place within the body in certain states of disease; hence, according to Thudichum, it occurs in gall-stones (p. 588).

The easiest mode of preparing cholic acid is to boil the resinous acids precipitated by ether from an alcoholic solution of bile (p. 585) with baryta-water in a retort having its neck directed upwards, adding as much hydrate of barium as will dissolve in the boiling liquid, and continuing the ebullition for about twelve hours. The crystalline mass of hydrate and cholate of barium obtained on cooling, is decomposed by hydrochloric acid, the cholic acid then separating as a glutinous resin, while chloride of barium remains in solution. The cholic acid is suffered to remain in the liquid till it is completely solidified, a few drops of ether being added to accelerate the process, after which it is washed with cold water, dissolved in boiling alcohol or ether, and the solution left to crystallise. Potash may be used in the preparation instead of baryta, but it is less advantageous.

Cholic acid has a bitter taste, with slight saccharine aftertaste. It crystallises in two different forms, and with different quantities of crystallisation-water, according as it is deposited from alcohol or ether.

a. $2C^{24}H^{40}O^5.5H^2O$. This hydrate is deposited from boiling alcohol. It forms tetrahedral or more rarely octahedral crystals, belonging to the dimetric system. Observed combinations $\frac{P}{2} . \infty P$ and $P . \infty P\infty$. Ratio of principal to secondary axis

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* Cholic acid is the name originally proposed by Demarçay. Strecker afterwards altered it to cholalic acid, reserving the term cholic acid for the nitrogenous bile-acid which yields this acid, together with glycocine, by decomposition; but it is more systematic to call this nitrogenised acid glycocholic acid, and retain Demarçay's name for the non-azotised acid.

= 0·7946; P : P, in the terminal edges = 116° 114′; in the lateral edges = 96° 40′. The crystals are colourless, very brittle, and have a glassy lustre. In a dry atmosphere they lose their water of crystallisation, and become opaque. They dissolve in 750 pts. of boiling water, in 4000 pts. of cold water, in 20·8 pts. of cold alcohol of 70 per cent., and are very soluble in boiling alcohol. The alcoholic solution becomes milky on addition of water, and after a while deposits shining needles. 1 pt. of cholic acid (? the $\frac{5}{2}$-hydrate), dissolves in 27 pts. of ether.

b. $C^{24}H^{40}O^5.H^2O$. This hydrate is deposited from boiling ether, in crystals belonging to the trimetric system, exhibiting the combination ∞P . ∞P̆∞ . P, but having the aspect of monoclinic crystals, in consequence of the predominance of one half of the P-faces in the same zone. Ratio of brachydiagonal, macrodiagonal, and principal axis = 0·6036 : 1 : 0·3752. Inclination of faces, P : P = 71° 58′; 119° 36′, and 144° 39′; P : ∞P = 125° 39′; ∞P : ∞P = 62° 15′; ∞P̆∞; ∞P = 148° 53′. (H. Kopp.)

The two hydrates above described seem to contain different modifications of cholic acid; the dimetric variety gives off all its water at 100° C., and may then be heated to 170° without decomposing, whereas the trimetric modification is not easily dehydrated at 100°, and melts, with decomposition, at 150°. The two modifications, however, yield the same salts, and are easily converted one into the other.

Cholic acid heated to 200° C. gives off the elements of 1 at. water, and is converted into choloïdic acid: $C^{24}H^{40}O^5 - H^2O = C^{24}H^{38}O^4$, and at 290° it is converted in like manner into dyslysin: $C^{24}H^{40}O^5 - 2H^2O = C^{24}H^{36}O^3$. By distillation, it yields a yellowish, very acid oil, with only a very slight carbonaceous residue. The oil is soluble in ether and in alkalis: the alkaline solution precipitates metallic salts.

Cholic acid dissolves easily in caustic alkalis, also in hot solutions of alkaline carbonates, expelling the carbonic acid. The CHOLATES, $C^{24}H^{39}MO^5$, have a very bitter taste. sometimes slightly saccharine; they are soluble in alcohol; those of the earth-metals and heavy metals are sparingly soluble in water, and may be obtained by precipitation.

Cholic acid and its salts give with sulphuric acid and sugar the reaction already described as Pettenkofer's test for bile (p. 586).

Cholate of Ammonium, obtained by passing ammonia-gas into an alcoholic solution of cholic acid and precipitating by ether, forms slender needles, soluble in water. It is decomposed by prolonged exposure to the air, with loss of ammonia, more quickly when boiled with water.

Cholate of Barium, $C^{24}H^{39}BaO^5$, is obtained by dissolving the acid in baryta-water, precipitating the excess of baryta by carbonic acid, and concentrating the filtrate, as a crystalline pellicle mammellated on the surface, silky in the interior. It dissolves in 30 pts. of cold, 23 pts. boiling water, and in a smaller quantity of alcohol. The solutions are decomposed by a continued stream of carbonic acid. A concentrated solution of cholate of potassium yields a white flaky precipitate with chloride of barium.

Cholate of Calcium, is precipitated in thick clots, which crystallise from ether. The *copper-salt* is a bluish-white precipitate. The *lead-salt* is white, sparingly soluble in water, soluble in alcohol and acetic acid. The *manganese-salt* is a semi-crystalline flocculent precipitate. The *mercury-salts* are white precipitates, which dissolve slowly by ebullition.

Cholate of Potassium, precipitated by ether from its alcoholic solution, or obtained by spontaneous evaporation, forms slender needles. From its aqueous solution it is precipitated by strong potash. *Cholate of sodium* resembles the potassium-salt.

Cholate of Silver is obtained as a white precipitate, which partly dissolves on boiling, and crystallises as the solution cools. It blackens slightly at 100° C., dissolves easily in alcohol.

CHOLOCHROME. The general name for the colouring matters of bile; it includes the ordinary brown bile-pigment called cholophæin or biliphæin; a green substance, cholochloin or biliverdin, produced by oxidation of cholophæin; and cholofulvin or bilifulvin, a yellow substance found in thickened ox-bile. These substances were first examined by Berzelius (Lehrb. d. Chem. ix. 281), afterwards by Simon, Plattner, Schmid, Scherer and Heintz (Gerh. *Traité*, iv. 532), and Thudichum (*British Medical Journal*, July 14th, 1860).

Cholophæin, or the brown pigment, is contained in bile and in the intestinal canal, and is the substance to which excrements owe their colour. In certain states of disease it occurs in the blood, the serous fluids, the urine, and other liquids of the organism, and is the cause of the yellow colour of the skin and the cornea in jaundice. It is most conveniently prepared from gall-stones, of which it sometimes forms the chief part, by exhausting them with alcohol, ether, and boiling water; washing the residue with hydrochloric acid, then with water; dissolving it in a weak solution of carbonate of sodium; and precipitating by an acid. As the cholophæin is very apt to pass into the green pigment by oxidation, it is best to perform all these operations in an atmosphere of hydrogen (Heintz). From human gall-stones cholophæin may also be extracted by benzene or by chloroform. (Thudichum.)

Cholophæin recently precipitated is a brown amorphous substance, becoming darker when dry. It is infusible, insoluble in boiling water; soluble in boiling alcohol, the solution gradually turning green by contact with the air. Hydrochloric acid dissolves it in small quantity, acquiring a blue colour. On adding excess of ammonia, the liquid immediately acquires a greenish-yellow colour, which is changed to red by nitric acid.

Cholophæin contains, according to Heintz's analysis, 60·9 per cent. carbon, 6·05 hydrogen, and 9·1 oxygen, whence may be deduced the empirical formula, $C^{16}H^{18}N^2O^{4\cdot5}$ (61·9 C, 58 H, 9·0 N, and 23·2 O).

Caustic alkalis and alkaline carbonates dissolve cholophæin with brownish-yellow colour: the ammoniacal solution yields a brown flaky precipitate with chloride of barium or chloride of calcium. A solution of cholophæin in very dilute alcoholic potash assumes a green colour on addition of hydrochloric acid; and if nitric acid be then added drop by drop, a fine blue colour is produced, which lasts a long time.

Cholochloïn or *Biliverdin.*—This green pigment is produced by the oxidation of cholophæin. An alkaline solution of the latter gradually oxidises by exposure to the air, and, if then treated with acids, yields a green precipitate. Cholochloïn exists ready formed in ox-bile, and is abundant in that of birds, fishes, and amphibia.

Thudichum obtains the green pigment by allowing bile to stand in well-closed bottles for two years, whereupon a putrefactive decomposition ensues (p. 587), and cholochrome is precipitated, together with cholic acid and other substances. The precipitate, after decantation of the liquid, is put into a calico-bag and washed with water as long as the liquid will pass through; then boiled with alcohol and washed on a filter with large quantities of that liquid, which removes cholic acid and its salts, also fats and fatty acids. The colouring matter then remains, mixed with mucus, from which it may be freed by solution in carbonate of sodium. The alkaline solution, treated with hydrochloric acid, throws down a substance of a fine green colour, which however is probably still somewhat impure.

Cholochloïn is destitute of taste and odour. It does not melt when heated, but decomposes at a high temperature, leaving a large quantity of carbon. It is insoluble in cold, slightly soluble in boiling water; easily soluble in alkalis, also in alcohol.

According to Heintz, cholochloïn contains 60·04 per cent. C, 5·84 H, 8·53 N, and 25·59 O, whence is deduced the empirical formula $C^8H^9NO^{2\cdot5}$, requiring 60·38 C, 5·66 H, 8·80 N, and 25·16 O. Cholochloïn forms with baryta a green amorphous compound, containing 27·3 per cent. baryta.

The formulæ of cholophæin and cholochloïn, as deduced from their analyses, are very uncertain. Thudichum found 60 to 62 per cent. carbon in cholophæin from gall stones, and as much as 66 per cent. in that prepared from bile. Probably both modifications contain the same number of carbon-atoms, the green compound containing more oxygen than the brown: thus cholophæin = $C^8H^9NO^{2\cdot25}$, and cholochloïn $C^8H^9NO^{2\cdot5}$, or possibly $C^8H^9NO^2$ and $C^8H^9NO^3$.

CHOLOCHROMIC ACID. When nitric acid containing nitrous acid, is added to a dilute solution of cholochrome (either brown or green) in an aqueous alkali, the colour of the liquid changes to green, blue, violet, red, and finally to yellow. These changes of colour are connected with the formation of a non-azotised acid, which, according to Thudichum, may be obtained by passing nitrous acid vapours into water in which cholophæin is suspended. Effervescence then takes place, arising from evolution of nitrogen; the colour of the bile-pigment changes from brown to red; and on subsequently shaking it up with ether, a red solution is obtained, which on evaporation leaves a pink syrupy residue, consisting of the non-azotised acid, *cholochromic acid*. It dissolves easily in chloroform, and the solution, when evaporated in an atmosphere of coal-gas, and afterwards left to stand for some days in a flask filled with the same gas, deposits the acid, partly in flat rhombic octahedrons, partly in groups of radiating needles, partly as an amorphous mass.

Thudichum assigns to this acid the formula $C^{16}H^{18}O^7$, or $C^8H^9O^{3\cdot5}$. It should perhaps be $C^8H^8O^3$, in which case its formation from cholophæin might be represented by the equation:

$$C^8H^9NO^2 + HNO^2 = C^8H^8O^3 + N^2 + H^2O,$$

the reaction being that of nitrous acid on an amic acid (p. 168).

Cholochromic acid is nearly insoluble in cold water, but easily soluble in alcohol:

the solution has an acid reaction, and precipitates metallic salts. The lead-salt has a red, the silver-salt a pink colour.

CHOLOÏDANIC ACID. $C^{16}H^{24}O^{7}$ (?)—The residue in the retort obtained in treating choloïdic acid with nitric acid, separates on cooling into two layers, the upper of which is crystalline, and consists of choloïdanic acid. The crystalline crust is drained on a funnel containing pounded glass, and purified by recrystallisation from boiling water. Should the residue in the retort be merely a resinous mass, it must be further subjected to the action of nitric acid, which will finally convert it into the crystalline acid.

Choloïdanic acid crystallises in long hair-like prisms, which, after drying on paper, have the aspect of asbestos. It is nearly insoluble in cold water, and but sparingly soluble in boiling water; easily soluble in alcohol: the solutions are acid. It does not lose weight at 100° C.; but at a higher temperature it blackens and gives off an acrid acid vapour. It dissolves without alteration in hot nitric or hydrochloric acid.

Choloïdanic acid requires a large quantity of alkali to saturate it. The choloïdanates of the alkali and alkaline earth-metals are soluble in water; the rest are insoluble or sparingly soluble. They are all decomposed by washing with water.

CHOLOÏDIC ACID. $C^{24}H^{38}O^{4}$.—This acid was discovered by Demarçay, and has been further examined by Theyer and Schlosser and by Strecker (see references, p. 926). It is produced by the dehydration of cholic acid at 200° C., and, according to the observations of Gorup-Besanez and of Thudichum (p. 587), is one of the products of the putrefaction of bile: hence also it is found in gall-stones. It may be prepared directly from bile by boiling that liquid, dissolved in 12 to 15 pts. water, with excess of hydrochloric acid for three or four hours, and leaving the liquid to cool. Choloidïc acid then collects at the bottom in a solid mass, which must be several times melted with water to remove the hydrochloric acid, then pulverised, dissolved in a small quantity of alcohol, shaken up with ether to free it from cholesterin and margaric acid, and finally evaporated to dryness over the water-bath. If the action of the hydrochloric acid be too long continued, dyslysin is obtained instead of choloïdic acid (Demarçay). Choloïdic acid is likewise obtained by digesting bile with oxalic acid. (Theyer and Schlosser.)

Choloïdic acid is a white non-crystalline substance, which melts in boiling water without dissolving to a sensible amount. After drying it requires a heat of more than 150° C. to melt it. It is very soluble in alcohol; water renders the solution milky, and separates the acid in the form of a resin; the solution has an acid reaction. It is sparingly soluble in ether.

Choloïdic acid unites with bases and decomposes carbonates with aid of heat. The choloïdates of the alkali-metals are soluble in water and alcohol, insoluble in ether; they have a pure bitter taste without any sweetish after-taste. By evaporation they are obtained in the form of gummy masses. The salts of the earth-metals and heavy metals are insoluble or sparingly soluble in water, insoluble in alcohol, and are obtained in the form of plastic precipitates. The *barium-salt*, $C^{24}H^{37}BaO^{4}.2H^{2}O$ (at 120° C.) is insoluble in water and amorphous. The *silver-salt*, $C^{24}H^{37}AgO^{4}$ (at 100° C.), is a bulky white precipitate, which undergoes considerable contraction and coloration by drying.

Choloïdic acid is oxidised by strong nitric acid, yielding a great number of products. If 1 vol. choloïdic acid be treated in a tall vessel with 4 or 5 vol. strong nitric acid, the whole distilled to one-fifth, after the first violent action has subsided, cohobating if necessary, and the liquid, when the action has ceased, diluted with twice its bulk of water and again distilled, a distillate is obtained having a very acrid suffocating odour, arising from the presence of a heavy oil, consisting of nitrocholic acid, $CH^{2}N^{4}O^{5}$ (?), and cholacrol, while on the surface of the watery liquid there floats a light oil, which is a mixture of acetic, valeric, caprylic, and capric acid. The residue in the retort is a yellowish mixture of oxalic, cholesteric, and choloïdanic acids. (Redtenbacher, Ann. Ch. Pharm. lvii. 145.)

CHOLONIC ACID. $C^{26}H^{41}NO^{5}$. (Strecker, Ann. Ch. Pharm. lxvii. 1.—Mulder, *Untersuch. über die Galle.*—Gerh. iv. 722.)—This acid, which is homologous with glyco-hyocholic acid ($C^{27}H^{43}NO^{5}$), is produced by the action of strong acids upon glycocholic acid, from which it differs only by the elements of 1 at. water.

When a solution of glycocholic acid in strong sulphuric or hydrochloric acid is heated, it becomes turbid and yields oily drops, which solidify and become resinous on cooling; and by treating this resinous product with baryta-water, and decomposing the insoluble barium-salt with hydrochloric acid, cholonic acid is separated, and may be obtained in shining needles by crystallisation from alcohol.

Cholonate of Sodium, $C^{26}H^{40}NaNO^{5}$, is crystallisable.

In preparing cholonic acid by the action of hydrochloric on glycocholic acid, another acid is sometimes formed containing 1 at. H^2O less. (Strecker.)

CHONDRIN. $C^{16}H^{26}N^2O^7$. (J. Müller, Pogg. Ann. xxxviii. 305.—F. Simon, J. Chem. méd. i. 108.—Vogel, J. pr. Chem. xxi. 426.—Hopp, *ibid.* lvi. 129).—A substance resembling gelatin in many of its properties, and long confounded with it: its separate identity was first established by Müller.

Chondrin, like gelatin, does not occur ready formed in the organism, but is produced by boiling certain tissues with water. All permanent cartilages in a healthy state yield chondrin when boiled with water; so does bone-cartilage or ossein before ossification; but bone-cartilage after ossification yields gelatin by boiling: so likewise do the tendons, skin, calves' feet, hartshorn, isinglass, and fish scales; also the permanent cartilages when they become ossified by disease.

Chondrin may be prepared by boiling the cartilages of the ribs, larynx, or joints with water for about forty-eight hours, evaporating the liquid to a jelly, and treating this residue with ether to free it from fat. The cornea of the eye yields the same substance.

Chondrin, when dried, is a hard, horny, diaphanous substance, which softens to a jelly in cold water, and dissolves completely in boiling water; it is insoluble in alcohol and in ether. The aqueous solution, when boiled for a long time, yields a substance perfectly soluble in cold water, but resembling chondrin in all its other reactions.

Nearly all acids, even organic acids, precipitate chondrin from its aqueous solution. The precipitate formed by hydrochloric, sulphuric, nitric, phosphoric, phosphorous, chloric, or iodic acid, redissolves easily in excess of the acid; that formed by sulphurous, pyrophosphoric, hydrofluoric, carbonic, arsenic, acetic, tartaric, oxalic, citric, lactic, or succinic acid does not redissolve in excess of the acid employed. Strong sulphuric acid dissolves chondrin, forming a syrupy liquid, which, when diluted with water and boiled, yields leucine without glycocine (Hopp). Sulphurous acid slowly decomposes chondrin. Nitric acid, by prolonged action, converts it into *xantho-proteic acid.*

Alum, sulphate of aluminium, acetate and subacetate of lead, sulphate of copper, ferrous and ferric sulphates, ferric chloride, mercurous and mercuric nitrates, produce copious precipitates in a solution of chondrin, soluble for the most part in excess of the reagent. Ferrocyanide of potassium produces no precipitate. The precipitates formed by acetic acid, alum, and sulphate of aluminium dissolve completely on adding a sufficient quantity of acetate of potassium (or of sodium) or common salt. The precipitate formed by ferric sulphate redissolves on heating the liquid. Mercuric chloride does not precipitate a solution of chondrin; sometimes a slight turbidity is produced, owing apparently to the presence of a little gelatin.

Chondrin is especially distinguished from gelatin by its precipitation by alum, sulphate of aluminium, acetate of lead, the sulphates of iron and sulphate of copper, and by its non-precipitation by mercuric chloride. (See GELATIN.)

The aqueous solution of chondrin treated with chlorine, yields a precipitate containing $C^{16}H^{23}ClN^4O$ (?) (Schröder.)

By dry distillation chondrin yields the same products as gelatin (*q. v.*)

Mulder (Ann. Ch. Pharm. xxviii. 328) found in chondrin from human cartilage, 49·3 per cent. C, 6·6 H, 14·4 N, and 0·4 sulphur. Schröder also found in chondrin from the cartilages of the cow, 49·3 carbon and 6·6 hydrogen.

CHONDRODITE. *Hemiprismatic Chrysolite, Maclureite, Humite, Brucite* (in part).—A silicate of magnesium containing fluorine; sometimes occurring in small implanted crystals, but more frequently in crystalline grains or masses of somewhat granular structure, imbedded in granular limestone, as at Pargas in Finland, at Aker and Gulsjö in Sweeden, in Sussex County, New Jersey, in Orange County, New York, and other localities. The variety called *humite* is from Vesuvius, where it occurs in ejected masses of a kind of granite rock, together with olivine, mica, and magnetite.

The crystals belong to the trimetric system, and are often hemihedral in octahedral planes, producing forms of monoclinic character; $\infty P : \infty P = 94° 26'$. They are of three types, in which the axes have the following ratios:

	Macrodiagonal.		Brachydiagonal.		Principal axis.
Type I.	1·4678	:	1	:	1·0805
Type II.	1·5727	:	1	:	1·0805
Type III.	1·4154	:	1	:	1·0805

Compound crystals also occur. Cleavage indistinct. Specific gravity 3·118 to 3·22. Hardness 6 to 6·5. Colour yellow or brown, inclining to red and green, with waxy or glassy lustre; more or less translucent. It is scarcely fusible before the blowpipe, gives the reactions of fluorine when heated with sulphuric acid, and with fluxes the reactions of iron and silica. Dissolves in hydrochloric acid, with separation of gelatinous silica.

Analyses.—1. Seybert (Sill. Am. J. v. 336.—2, 3, 4. Rammelsberg (*Mineralchemie*, p. 443).—5. Fischer (Sill. Am. J. [2] ix. 85.—6, 7, 8. Rammelsberg (*loc. cit.*):

	SiO^2.	Mg^2O.	Fe^2O.	Fe^4O^3.	F.	
1. New Jersey . . .	32·66	54·00	—	2·33	—	HF 4·09; H^2O 1·0; K^2O 2·11
2. „ *yellow* . .	33·06	55·46	3·65	—	7·60	= 99·77
3. Pargas, *yellow* . .	33·10	56·61	2·35	—	8·69	= 100·75
4. „ *grey* . . .	33·19	54·50	6·75	—	9·69	= 104·13
5. New Jersey, *red* . .	33·35	53·05	5·50	—	7·60	= 99·50
6. *Humite*, type I. . .	34·80	60·08	2·40	—	3·47	= 100·75
				Ca^2O.		
7. „ type II. . .	33·26	57·94	2·30	0·70	5·04	Al^4O^3 = 1·06 = 100·38
8. „ type III. . .	36·67	56·83	1·67	—	2·61	= 97·78

These analyses lead to the formula $8Mg^2O.3SiO^2 = Mg^{16}Si^3O^{14} = 2Mg^2O.3Mg^4SiO^4$, wherein part of the oxygen is replaced by fluorine; or the mineral may be represented as made up of the two compounds:

$$Mg^{16}Si^3F^{28}, \text{ or } 16MgF.3SiF^4 = A$$

and:

$$Mg^{16}Si^3O^{14}, \text{ or } 8Mg^2O.3SiO^2 = B$$

in various proportions, namely:

Chondrodrite from Finland and North America $= A + 12B$
Humite from Vesuvius, type I. $= A + 18B$
„ „ type II. $= A + 27B$
„ „ type III. $= A + 36B$

Chondrodite occurs altered to serpentine at Sparta, New Jersey, with spinel and mica. (Dana, ii. 186.)

CHONDROGEN. A name applied to the tissues which yield chondrin when boiled with water, or rather to the substance which may be regarded as the basis of these tissues.

CHONDROITES. Concretions occurring in the cavities and channels of the animal body which are lined with mucous membranes, especially in the nose, gullet, tonsils, and bronchiæ: they are produced, under abnormal circumstances, from the secretion of these membranes, their nucleus being sometimes a solid body accidentally lodged in these cavities. They contain very variable quantities of water and animal matter, together with 50—80 per cent. of phosphate of calcium, 6—20 per cent. carbonate of calcium, 8—12 per cent. carbonate of magnesium, and small quantities of soluble salts. (Handw. d. Chem. ii. [2] 1196.)

CHONICRITE. A dense non-crystalline mineral from Elba, of specific gravity 2·91, hardness 3. Fracture conchoïdal. White. Translucent at the edges. Melts with tolerable facility to a greyish-white glass, evolving bubbles of gas at the same time; blue glass with cobalt-solution. Dissolves slowly in borax, yielding a glass slightly coloured by iron. Easily decomposed by concentrated hydrochloric acid, with separation of silica, not in the usual gelatinous state. According to Kobell's analysis, it contains 12·6 lime, 22·5 magnesia, 1·46 ferrous oxide, 17·12 alumina, 35·7 silica, and 9·0 water, a composition which may be approximately represented by the formula: $9(2M^2O.SiO^2).2(2Al^4O^3.3SiO^2) + 12\,aq.$, which by substituting $al = \frac{2}{3}$ Al, may be reduced to $3M^4SiO^4.2al^4SiO^4 + 4$ aq. (*Rammelsberg's Mineralchemie*, p. 858). Dana regards chonicrite as a variety of pyrosclerite (*q. v.*)

CHRISMATIN. A viscid translucent resin from Wettin near Halle, where it occurs as a coating on calcspar in a fissure. It has a shining lustre, and varies in colour from yellow to olive-green. Burns with flame and without odour. (Germar, Deutsche geol. Zeitschr. i. 40.)

CHRISTIANITE. See PHILLIPSITE.

CHROMATES. Chromic acid unites with nearly all bases. The salts are for the most part easily crystallisable and isomorphous with the corresponding sulphates. The chromates of the alkali-metals, and of strontium, calcium, and magnesium, are soluble in water: the others are insoluble, or sparingly soluble.

With the alkali-metals, chromic acid forms two series of salts, namely, neutral or normal chromates, $MCrO^2$, or $M^2O.Cr^2O^3$, which are yellow, and acid chromates, commonly called bichromates, $2MCrO^2.Cr^2O^3$, or $M^2O.2CrO^3$, which have an orange-red colour: a hyperacid chromate, or trichromate of potassium, $KCrO^2.Cr^2O^3$, or $K^2O.3Cr^2O^3$, is likewise known. These salts are produced, either by direct saturation of the base with chromic acid, or by igniting chromic oxide with an alkali and a nitrate or other oxidising agent.

The insoluble chromates are obtained by precipitation. Most of them are basic. Those which contain 3 at. basic metal to 1 at. chromium, may be called orthochromates, M^3CrO^3, or $3M^2O.Cr^2O^3$, the ordinary neutral chromates $MCrO^2$, which differ from them by M^2O, being metachromates.

A solution of an alkaline chromate gives with a salt of *barium*, *lead*, or *bismuth*, a yellow precipitate: with *mercurous* salts a brick-red, and with *silver*-salts, a red-purple precipitate: all these precipitates are soluble in nitric acid. Chromates boiled with excess of *hydrochloric* acid, yield a green solution of sesquichloride of chromium. A chromate of alkali-metal boiled with sulphuric acid and a reducing agent, such as *sugar*, *alcohol*, or *tartaric acid*, yields a purple or a green solution of a chromic alum. Chromates heated with *sulphuric acid and common salt*, give off yellowish-red vapours of oxychloride of chromium. The chromates of the less basic metals give off oxygen when ignited, and leave chromic oxide: the acid chromates of the alkali-metals leave a mixture of chromic oxide and neutral chromate. Insoluble chromates fused with *nitre*, yield chromate of potassium, which may be dissolved out by water.

Chromates in solution have a bitter metallic taste, and a poisonous action.

Chromates of Ammonium.—The *neutral salt* $(NH^4)CrO^2$, is obtained by evaporating a mixture of chromic acid with excess of ammonia, or by decomposing chromate of barium with sulphate of ammonium. Hirzel (Zeitschr. f. Pharm. 1852, p. 24), gradually adds oxychloride of chromium to excess of ammonia, and evaporates the solution at 60° C. Chromate of ammonium then crystallises out, and may be purified by recrystallisation. It forms lemon-yellow needles, permanent in the air; has a pungent taste and alkaline reaction. It is very soluble in water. Leaves chromic oxide when ignited.

Acid salt, $2NH^4CrO^2.Cr^2O^3$, or $(NH^4)^2O.2Cr^2O^3$.—Obtained by dividing a solution of chromic acid into two parts; saturating one with ammonia, then adding the other, and evaporating the whole over sulphuric acid. It forms orange-coloured crystals, permanent in the air, soluble in water, and yielding green chromic oxide when ignited. (Richmond and Abel, Chem. Soc. Qu. J. iv. 199.)

Darby (*ibid.* i. 20), by partially saturating chromic acid with ammonia and evaporating to the crystallising point, obtained a compound of ammonia with chromic anhydride $2NH^3.Cr^2O^3$, which may be regarded as a *chromamate of ammonium*, $\left.\begin{matrix}NH^2(Cr^2O^2)''\\ NH^4\end{matrix}\right\}O$, analogous to sulphamate of ammonium, $\left.\begin{matrix}NH^2(SO^2)''\\ NH^4\end{matrix}\right\}O$.

Hyperacid salt, $2NH^4CrO^2.5Cr^2O^3 + 10\,aq.$, or $(NH^4)^2O.6Cr^2O^3 + 10\,aq.$—Brown-yellow, very efflorescent salt, obtained in ill-defined crystals by evaporating a solution of chromic acid half neutralised with ammonia. (Rammelsberg, Pogg. Ann. xciv. 507.)

A compound of *chromic anhydride and sal-ammoniac*, $NH^4Cl.Cr^2O^3$, is obtained by adding oxychloride of chromium to a strong solution of sal-ammoniac, in crystals having the same form and aspect as the corresponding potassium-compound, but much more soluble in water. (Péligot, Ann. Ch. Phys. [2] lii. 267.)

Chromate of Barium.—The *neutral chromate*, $BaCrO^2$, is prepared by precipitating chromate of potassium with chloride of barium or baryta-water. It is insoluble in water, but dissolves, with reddish-yellow colour, in nitric, hydrochloric, or excess of chromic acid, and is precipitated from the solution by ammonia. It is decomposed by alkaline carbonates and sulphates, even at ordinary temperatures, and more quickly when heated. It is used as a pigment called *yellow ultramarine*.

Acid salt, $2BaCrO^2.Cr^2O^3$, or $Ba^2O.2Cr^2O^3$.—A concentrated solution of the neutral salt in chromic acid is decomposed by dilution, part of the salt being precipitated, while an acid salt remains in solution, and may be obtained by evaporation in yellowish-brown stellate crystals, containing $Ba^2O.2Cr^2O^3 + 2\,aq.$, which dissolve slowly in water, with separation of the neutral salt. (Babo, J. pr. Chem. lx. 60.)

Chromate of Bismuth.—When a solution of nitrate of bismuth is added to a moderately concentrated solution of acid chromate of potassium, leaving the latter slightly in excess, an egg-yellow, flocculent precipitate is formed, which afterwards becomes dense and crystalline. It consists of $3Bi^2O^3.2Cr^2O^3$ or $7Bi^2O^3.4Bi'''Cr^3O^6$. It is insoluble in water, may be dried without decomposition at 100° to 125° C., but acquires a dark green colour when ignited, and retains this colour after cooling. It dissolves in nitric or hydrochloric acid, forming a deep yellow liquid, which becomes turbid on dilution, from precipitation of basic nitrate or chloride of bismuth. If it be treated with a small quantity of acid, a yellow salt remains undissolved, consisting of $Bi^2O^3.2Cr^2O^3$ or $Bi^2O^3.4Bi'''Cr^3O^6$. The latter may also be obtained by precipitating acid chromate of potassium with a slightly acid bismuth-solution (J. Löwe, J. pr. Chem. lxvii. 288, 463). According to Pearson (*ibid.* lxviii. 255), the precipitate formed in the latter case is $Bi^2O^3.Cr^2O^3$, and is perfectly insoluble in water, so that it may be conveniently used for the estimation of bismuth.

Chromate of Cadmium.—A basic salt, $5Cd^2O.2Cr^2O^3 + 8aq.$, or $3Cd^2O.4CdCrO^2 + 8aq.$, is obtained as an orange-yellow precipitate, on mixing a cadmium-salt with neutral chromate of potassium. On adding ammonia, the salt $2NH^4CrO^2.(NH^3Cd)^2O + 2aq.$ is obtained, which crystallises in transparent, bright-yellow, six-sided pyramids, decomposing when exposed to the air or immersed in water.

Chromate of Calcium.—The *neutral* salt $CaCrO^2 + aq.$, is obtained by dissolving carbonate of calcium in aqueous chromic acid, or as a light yellow precipitate by mixing concentrated solutions of chromate of potassium and chloride of calcium. It is moderately soluble in water, insoluble in alcohol; gives off its water at 200° C., and is afterwards very sparingly soluble. The anhydrous salt is used as a pigment. The *acid-salt* obtained by dissolving the neutral salt in aqueous chromic acid and evaporating, forms red deliquescent crystals, containing $2CaCrO^2.Cr^2O^3 + 3aq.$

Chromate of Calcium and Potassium, $(KCa)Cr^2O^4 + aq.$, obtained by saturating acid chromate of potassium with hydrate of calcium, forms lemon-yellow, silky crystals.

Chromate of Cerium, $CeCrO^2$, is deposited as a yellow powder from a solution of carbonate of cerium in chromic acid. The filtrate yields on evaporation an acid salt in red prisms, soluble in water.

Chromate of Chromium.—The brown oxides of chromium intermediate between the sesquioxide Cr^4O^3, and chromic anhydride, Cr^2O^3, may be regarded as compounds of these two in various proportions, that is, as chromates of chromium. (See **Chromium, Oxides of.**)

Chromate of Cobalt.—Solutions of cobalt-salts form with chromate of potassium, a light red-brown precipitate containing, according to Sarzeau and Malaguti (Ann. Ch. Phys. [3] ix. 431), $Co^2CrO^3 + 2aq.$, which is the formula of an orthochromate.

Chromates of Copper.—When impure cupric hydrate is immersed in a strong solution of chromic acid, a brown solution is formed which deposits a brown powder, probably a tetrabasic salt, $4Cu^2O.2Cr^2O^3$, or $2Cu^2O.4CuCrO^2$ (Dröge, Ann. Ch. Pharm. ci. 89). The solution filtered through asbestos, and evaporated over oil of vitriol, yields, after a while, green crystals, consisting, according to Kopp (*ibid.* lvii. 386), of cupric sulphate in which part of the sulphuric acid is replaced by chromic acid (H^2SO^4 by $H^2Cr^2O^4$, or S by Cr^2). The mother-liquor decanted therefrom, is free from sulphuric acid, and yields by evaporation, acid cupric chromate, $2Cu^2CrO^2.Cr^2O^3 + 2aq.$, in brown-black, deliquescent crystals, soluble in alcohol and in ammonia. The aqueous solution deposits on boiling a brown insoluble salt. The crystals give off their water at 100° C., and at a red heat the salt is completely decomposed. The tetrabasic salt above mentioned is deposited as a chocolate-brown precipitate, containing 5 at. water, on mixing a boiling solution of neutral chromate of potassium with basic sulphate of copper. (Malaguti and Sarzeau.)

An *ammonio-chromate of copper*, $5NH^3.Cu^2O.4CuCrO^2 + aq.$, is obtained in dark green prismatic crystals, by passing ammonia-gas into water in which tetrabasic chromate of copper is suspended, and cooling the liquid below 0° C. It soon gives off its ammonia when exposed to the air: and is resolved by water into insoluble basic chromate of copper, and a basic ammonio-chromate which dissolves in the water with emerald-green colour. The same basic ammonio-chromate is obtained by treating acid cupric chromate with ammonia.

Chromate of Copper and Potassium, $K^2O.3Cu^2O.3Cr^2O^3 + 3aq.$, or $CuHO.(KCu^2Cr^2O^6 + aq.$, is obtained by treating recently precipitated cupric hydrate with solution of acid chromate of potassium, or by mixing a solution of cupric sulphate with acid chromate of potassium, and gradually adding caustic potash. The product is a light brown powder, consisting of microscopic, translucent, six-sided tablets, nearly insoluble in water, but dissolving with deep green colour in ammonia or carbonate of ammonium. The solution, if saturated while hot, deposits on cooling green prisms having a strong lustre.

Chromate of Glucinum is a yellow insoluble precipitate.

Chromate of Iron.—Aqueous chromic acid digested with moist ferric hydrate, yields a brown solution, containing $Fe^4O^3.4Cr^2O^3$. The solution is not rendered turbid either by dilution or by boiling, and yields on evaporation a brown resinous residue, soluble in water and in alcohol. The *basic salt* is a brown powder, which is resolved by water into ferric oxide and chromic acid.

Chromates of Lead.—The neutral or metachromate, $PbCrO^2$, is found native as *Red-lead ore*, *Crocoisite*, or *Lehmannite*, in monoclinic prisms, in which the ratio of the orthodiagonal, clinodiagonal, and principal axis is as 1·041 : 1 : 0·96, and the inclination of the principal axis to the clinodiagonal, 77° 30′. The predominant faces are generally ∞P and $-P$. Cleavage most distinct parallel to ∞P. Specific gravity 5·9 to 6·1. Hardness 2·5 to 3. The crystals are translucent and of a yellow colour, with various shades of bright hyacinth-red; streak orange-yellow. Sectile. It occurs in decomposed gneiss or granite, at Nischne Tagilsk in the Ural, in Brazil, at Retzbanya in Hungary, at Moldawa in the Bannat, and in Luzon, one of the Phillippine Isles.

Neutral chromate of lead is obtained as a light yellow insoluble precipitate, by mixing a dilute solution of a neutral lead-salt with neutral or acid chromate of potassium; concentrated solutions yield an orange-yellow precipitate. It may also be obtained by decomposing sulphate or chloride of lead with chromate of potassium. It is insoluble in water, slightly soluble in nitric acid, easily in potash. At a moderate heat, it melts without decomposition to a brown mass, exhibiting a radiated structure when cold, and yielding a dark yellow, slightly hygroscopic powder. At a full red heat, it gives off oxygen, and is reduced to a mixture of basic chromate of lead and chromic oxide. Heated in a stream of hydrogen gas, it gives up 12 per cent. oxygen, and is reduced to a mixture of chromic oxide and metallic lead, which when heated in a stream of oxygen takes up 7 per cent. of that gas. (On the use of chromate of lead in organic analysis, see pp. 227, 232.)

Chromate of lead is much used as a pigment, known as **chrome-yellow**, also *lemon-yellow, Leipzig yellow, Paris yellow*, &c. The finer sorts are prepared by precipitation, the commoner kinds by decomposing carbonate, chloride, or sulphate of lead (obtained as a by-product in the preparation of alum-mordants), with chromate of potassium. According to Anthon, 100 pts. sulphate of lead require for decomposition 25 pts. of red chromate of potassium, and 100 pts. chloride of lead require 27 pts. of red chromate. Chrome-yellow exhibits various shades of red and yellow, according to its mode of preparation: it is often mixed with chalk, gypsum, heavy spar, clay, sulphate of lead, &c. *Cologne yellow* is a mixture of chromate and sulphate of lead with sulphate of calcium, obtained by precipitating a mixture of the nitrates of lead and calcium with a mixture of sulphate of sodium and chromate of potassium. It is not altered by exposure to air or light; sulphuretted hydrogen turns it brown; protochloride of tin and sulphurous acid reduce it; alkalis turn it orange or red, by formation of basic chromate of lead. It is used as an oil or water-colour, for lacquering, and may be mixed with many other colours without decomposition; with Prussian blue it forms a green mixture, called **chrome-green**, or **green cinnabar**. In calico-printing, chrome-yellow is formed on the fabrics themselves, by first steeping them in a solution of lead-salt, then in chromate of potassium. For dyeing silk and wool it is not so well adapted.

Basic Chromate of Lead.—A *dibasic* or *tetraplumbic chromate*, $2Pb^2O.Cr^2O^3 = Pb^2O.2PbCrO^2$, known in the arts as **chrome-red**, is produced from the neutral chromate by digesting it with caustic alkalis, or with levigated oxide of lead, or by boiling it in the recently precipitated state with neutral chromate of potassium, or by fusing it with nitre. It is of a deep orange or red colour, according to the mode of preparation. The finest vermilion-red chromate is formed when 1 pt. of chrome-yellow is thrown into 5 pts. of nitre in a state of fusion, and the resulting chromate of potassium, together with the excess of nitrate, dissolved out by water: the basic chromate of lead then remains in the form of a crystalline powder (Liebig and Wöhler). An orange pigment may be obtained very economically, by boiling the sulphate of lead, which is a waste product in making acetate of alumina from alum by means of acetate of lead, with a solution of chromate of potassium. The basic chromate of lead, forms a beautiful orange upon cloth, which is even more stable than the yellow chromate, not being acted upon by either alkalis or acids. One method of dyeing chrome-orange, is to fix the yellow chromate of lead in the calico, by dipping it successively in acetate of lead and acid chromate of potassium, and then washing it. This should be repeated, in order to precipitate a considerable quantity of the chromate in the calico. A milk of lime is then heated in an open pan; and when it is at the point of ebullition, the yellow calico is immersed in it, and instantly becomes orange, being deprived of a portion of its chromic acid by the lime, which forms a soluble chromate of calcium. At a lower temperature, lime-water dissolves the chromate of lead entirely, and leaves the cloth white.

A *sesquibasic* or *hexplumbic chromate*, $3Pb^2O.2Cr^2O^3 = Pb^2O.4PbCrO^2$, is found native as *Melanochroïte, Phœnicite*, or *Phœnikochroite*, at Beresof in the Ural, associated with crocoisite, vauquelinite, pyromorphite, and galena. It occurs in tabular crystals, apparently belonging to the trimetric system, reticularly interwoven; cleaving perfectly in one direction; also massive. Specific gravity 5·75. Hardness 3 to 3·5. It has a resinous or adamantine, glimmering lustre, cochineal or hyacinth-red colour, becoming lemon-yellow on exposure to the air. Streak brick-red. Subtranslucent or opaque.

A *chromate of lead and copper*, of analogous composition, viz. $\left.\begin{matrix}Pb\\Cu^4\end{matrix}\right\}{}^2O.4\begin{pmatrix}Pb^3\\Cu^4\end{pmatrix}CrO^2$, called *Vauquelinite*, occurs at Beresof, at Pont Gibaud in the Puy de Dôme, and with the crocoisite of Brazil, in monoclinic crystals, usually minute and irregularly aggregated; also reniform or botryoïdal, and granular; amorphous. Specific gravity 5·5 to 5·78. Hardness 2·5 to 3. It has a dark green to brown colour, sometimes nearly black, with adamantine or resinous lustre, often faint. Streak, siskin-green or brownish. Faintly translucent or opaque. Fracture uneven. Rather brittle. (Dana, ii. 360.)

CHROMATE OF LITHIUM, $LiCrO^2$, crystallises in orange-yellow, oblique rhombic prisms, easily soluble in water.

CHROMATE OF MAGNESIUM, $2MgCrO^4 + 7aq.$, obtained by evaporating a solution of magnesia in chromic acid, forms lemon-yellow crystals isomorphous with sulphate of magnesium. Specific gravity = 1·66 at 15° C.

Chromate of Magnesium and Ammonium, $Mg(NH^4)Cr^2O^4 + 3aq.$, is isomorphous with the corresponding sulphate.

CHROMATES OF MANGANESE.—A *manganic* salt, $3(Mn^4O^3.Cr^2O^3).Cr^4O^3 + 6aq.$, is precipitated on mixing sesquichloride of manganese with chromate of potassium. (Fairrie, Chem. Soc. Qu. J. iv. 300.)

A *basic manganous chromate*, $2Mn^2O.Cr^2O^3 + 2aq. = Mn^2O.2MnCrO^2$, is obtained as a crystalline precipitate on mixing manganous sulphate with neutral chromate of potassium. It is brown, translucent, and dissolves with orange-yellow colour in sulphuric and nitric acids (Warington, *L'Institut*, No. 513, p. 366.—Reinsch, Pogg. Ann. lv. 97). According to Fairrie, it contains chromic oxide.

CHROMATES OF MERCURY.—*Mercuric metachromate*, $HgCrO^2$, is obtained by boiling equal parts of chromic anhydride and yellow mercuric oxide in water, and gradually evaporating till the mercuric oxide disappears, and red crystals are formed in its place: the mother-liquor yields an additional quantity by concentration. It forms dark garnet-red rhombic prisms, becoming darker-coloured when heated. They are decomposed by water, even in the cold, and completely when heated, yielding free chromic acid and amorphous *mercuric orthochromate*, Hg^3CrO^3. They dissolve readily in hydrochloric acid, and potash added to the solution throws down yellow mercuric oxide, or perhaps the orthochromate. Strong nitric acid converts them, in the cold, into an amorphous yellow compound, a large portion however dissolving; moderately strong nitric acid and dilute sulphuric acid act in the same manner, excepting that a larger quantity of the yellow compound remains undissolved.

Mercuric orthochromate, Hg^3CrO^3, or $3Hg^2O.Cr^2O^3$, is obtained as a brick-red powder on adding mercuric nitrate to acid chromate of potassium; or by boiling yellow mercuric oxide with chromate of potassium (Millon). It is also produced, together with a less basic salt, by precipitating the mother-liquor of the metachromate with carbonate of sodium. On boiling the precipitate with soda-ley, an amorphous, yellow, heavy powder is precipitated, which appears to consist of $7Hg^2O.2Cr^2O^3$, or $Hg^2O.4Hg^3CrO^3$. The same salt appears also to be obtained by boiling recently precipitated mercuric oxide with acid chromate of potassium, till it is converted into a brick-red powder, washing this powder repeatedly by decantation, and heating it with moderately strong nitric acid. It dissolves in strong nitric acid only when recently precipitated; strong sulphuric acid, with aid of heat, converts it into white mercuric sulphate; hydrochloric acid does not dissolve it. (Geuther, Ann. Ch. Pharm. cvi. 244.)

A *tetrabasic mercuric chromate*, $4Hg^2O.Cr^2O^3$, or $3Hg^2O.2HgCrO^2$, of dark violet or brown colour, is said to be obtained by boiling red mercuric oxide with chromate of potassium. When equivalent quantities of basic mercuric chromate and solution of cyanide of mercury and potassium are boiled together for some time, oxycyanide of mercury separates first, and afterwards a compound containing $KHgCy^2$ and $HgCrO^2$. (Geuther.)

Mercurous chromate, $Hg^4O.Cr^2O^3 = HhgCrO^2$, is obtained as a brilliant red crystalline powder, by boiling the basic salt next to be described, with a small quantity of dilute nitric acid, or the double salt of cyanide of mercury and chromate of potassium with mercurous nitrate.

Basic mercurous chromate, $2Hg^4O.Cr^2O^3 = Hhg^2O.2HhgCrO^2$, is obtained as a brick-red powder by precipitating mercurous nitrate with chromate of potassium. Both these salts when heated, give off oxygen and mercury, and leave chromic oxide of a beautiful green colour.

CHROMATES OF MOLYBDENUM.—The neutral salt dissolves in water with yellow colour, and yields by spontaneous evaporation, white, scaly, needle-shaped crystals. The acid salt dries up to an amorphous brown mass. The solution of either salt mixed with ammonia yields a precipitate of basic chromate of molybdenum.

CHROMATE OF NICKEL.—Hydrate and carbonate of nickel dissolve in chromic acid with yellowish-red colour, forming an acid salt (Malaguti and Sarzeau). The solution of a neutral nickel-salt boiled with neutral chromate of potassium, yields an amorphous precipitate, consisting of $3Ni^2O.2NiCrO^2 + aq.$, and having the colour of Spanish tobacco. If this or the soluble salt be covered with ammonia, a heavy yellow-green crystalline powder, $3NH^3.NiCrO^2 + \frac{2}{3}aq.$ is formed, which is decomposed by air and water.

Chromates of Potassium.—Three of these salts are known, viz.:

Neutral chromate, monochromate, or metachromate of potassium	$K^2O.Cr^2O^3$, or $KCrO^2$
Acid or dichromate	$K^2O.2Cr^2O^3$, or $2KCrO^2.Cr^2O^3$
Hyperacid or trichromate . . .	$K^2O.3Cr^2O^3$, or $KCrO^2.Cr^2O^3$.

The neutral and acid salts are important articles of manufacture, being extensively used in dyeing and calico-printing, and for the preparation of chrome-yellow and chrome-red; also as oxidising agents: the acid salt is most used, because it contains a larger percentage of chromic acid.

The chromates of potassium are prepared by igniting chrome-iron ore, a compound of sesquioxide of chromium and protoxide of iron, in contact with alkalis and oxidising agents, and lixiviating the fused mass with water. A yellow solution is thus obtained, from which, by quick evaporation, the neutral salt is thrown down in yellow crystalline granules; and by redissolving this granular salt in water, and leaving the solution to evaporate slowly, the salt is obtained in regular crystals. The concentrated solution of the neutral chromate, treated with one of the stronger acids, yields the acid chromate; and by evaporating the solution to the crystallising point, picking out the crystals of acid chromate from the nitrate or other potassium-salt formed at the same time, and recrystallising several times, the acid chromate is obtained in large tabular crystals of an orange-red colour

The process first adopted for the preparation of chromate of potassium, was to calcine the ore with nitre; but it may be rendered more economical by substituting carbonate of potassium (pearlash) for a portion of the nitre; and still more by dispensing with the nitre altogether, and effecting the oxidation of the chromic oxide by means of air admitted into the reverberatory furnace in which the calcination takes place. But whether nitre be used or not, the oxidation is still found to be imperfect, because the alkali fuses into a thin liquid, and the chrome-iron ore, being very heavy, sinks to the bottom, and thus remains to a great extent unaltered, especially when the oxidation is effected by contact with the air, an inconvenience which is but imperfectly obviated even by continual stirring. But by adding lime to the mixture, as first proposed by Stromeyer, it is rendered less fluid, and a moderate amount of stirring then suffices to keep it well mixed, so that the oxidation takes place with much greater facility. It is found, indeed, that when lime is added, the nitre may be altogether dispensed with, and its place supplied by carbonate, sulphate, or chloride of potassium, which are cheaper. Mr. Tilghman has patented a process for the use of felspar as a source of alkali, 4 pts. by weight of that mineral being calcined in a reverberatory furnace, with 4 pts. of lime or an equivalent quantity of chalk, and 1 pt. of chrome-iron ore. Mr. Booth of Philadelphia subjects the chrome-iron ore to a preliminary ignition with coke or other carbonaceous material, whereby the iron is reduced to the metallic state, then removes the iron by means of dilute sulphuric acid, and subjects the chromic oxide thus purified, to calcination with alkali and nitre; by this means, the portion of oxygen which would be expended in converting the protoxide of iron into sesquioxide, is rendered available for the production of chromic acid. The production of sulphate of iron incidental to the process tends to defray the expense.

Jacquelain prepares acid chromate of calcium from chrome-iron ore, and converts that salt into acid chromate of potassium by double decomposition. The chrome-ore, after being ground to very fine powder and sifted, is mixed with chalk in rotating barrels, and the mixture is spread in a layer 1½ to 2 inches thick on the hearth of a reverberatory furnace, heated to bright redness for nine or ten hours, and stirred at least every hour. After this treatment, the mixture has a yellowish-green colour, dissolves in hydrochloric acid, and with the exception of a certain quantity of sand, consists essentially of *neutral chromate of calcium* ($CaCrO^2$) mixed with oxide of iron. This mass is ground to powder by millstones; the powder is stirred up with hot water, and sulphuric acid is added till a slight acid reaction becomes apparent. The neutral chromate of calcium is thereby converted into *acid chromate*. The liquid also contains sulphate of iron, which is precipitated in the same vessel by stirring up with chalk, which does not affect the chrome-salt. The precipitate having settled down, the clear solution of acid chromate of calcium containing a little sulphate is run off, and may be used, without further treatment, for preparing by double decomposition, acid chromate of potassium, chromate of lead, either neutral or basic, and chromate of zinc. To obtain acid chromate of potassium, the solution of acid chromate of calcium is treated with carbonate of potassium, which throws down carbonate of calcium in a form easy to wash, leaving acid chromate of potassium in solution, which may then be evaporated and crystallised. The chief advantages of this process are that it requires less stirring than the ordinary method, even when lime is used, and that it avoids the loss of alkali, which always ensues (to the amount of 9 or 10 per cent.) when the mixture of chrome-iron ore and potassium-salt is raised to a bright red heat. (For further details on the manufacture of alkaline chromates, see *Ure's Dictionary of Arts, Manufactures, and Mines*, i. 684; and *Richardson* and *Watts' Chemical Technology* i. [4] 59.)

a. *Neutral Chromate of Potassium*, $KCrO^2$.—This salt is obtained by neutralising the acid chromate with an alkali, or by igniting chrome-iron ore with excess of alkali (p. 936). It crystallises in double six-sided pyramids, belonging to the trimetric system, and isomorphous with sulphate of potassium: hence it is capable of crystallising with the latter in all proportions. It has a pale lemon-yellow colour, an alkaline reaction, and a cooling, persistently bitter taste: it is poisonous even in small doses. Specific gravity 2·705 (Kopp). 100 pts. of water at 15° C. dissolve 48½ pts. of this salt, and in boiling water it dissolves in all proportions. It possesses great colouring power, 1 pt. of it imparting a distinct yellow tint to 400,000 pts. of water, and a deep yellow colour to 20 pts. of nitre when crystallised therewith. It is insoluble in alcohol, and is precipitated by alcohol from its aqueous solution. The solution yields by evaporation, red crystals of the acid chromate, and the alkaline mother-liquor afterwards deposits yellow crystals of the neutral salt. The neutral chromate acquires a transient red colour when heated, melts at a higher temperature, and solidifies in the crystalline form on cooling. It is not decomposed by simple ignition, but when heated to redness in contact with charcoal, sulphur, sal-ammoniac, and other reducing agents, it forms chromic oxide together with a potassium-salt. It is decomposed by acids, even by carbonic acid, yielding the acid chromate of potassium. Sulphydric acid and sulphide of potassium decompose it, with formation of chromic hydrate; sulphurous acid forms at first brown oxide of chromium, then a chromic salt. According to Schweizer (J. pr. Chem. xxxix. 267), arsenious acid forms with it a gelatinous mass, which after drying at 100° C. contains $4K^2O.3Cr^4O^3.3As^2O^3.10H^2O$.

b. *Acid Chromate*, $K^2O.2Cr^2O^3 = 2KCrO^2.Cr^2O^3$. *Bichromate of Potash, Red Chromate of Potash.*—This salt is obtained by treating the solution of the neutral salt with one of the stronger acids, or by precipitating a solution of acid chromate of calcium with carbonate of potassium (p. 936). It separates by rapid evaporation as an orange-coloured crystalline powder, and by slower evaporation in splendid garnet-red tables or prisms, belonging to the triclinic system. It is permanent in the air, reddens litmus, has a cooling, bitter, and metallic taste. Its powerful oxidising properties cause it to exert a poisonous action on the animal economy, both internally and externally: the workmen engaged in its manufacture suffer greatly from malignant ulcers. It dissolves in 10 pts. of water at 15° C., much more abundantly in boiling water; it is insoluble in alcohol. It melts at a heat below redness to a transparent red liquid, which by slow cooling yields large fine crystals, having the same form as those obtained from the aqueous solution, but crumbling to powder at lower temperatures. At a white heat, it gives off oxygen, leaving neutral chromate mixed with chromic oxide. Heated with charcoal, it is reduced, with slight detonation; paper or calico saturated with the solution and dried burns like tinder when heated. Paper thus saturated acquires a darker colour by exposure to light, but remains unaltered in the dark: hence it may be used in photography. Heated with strong sulphuric acid it gives off oxygen (about 16 per cent. by weight), and yields water and potassio-chromic sulphate (chrome-alum).

$$K^2Cr^4O^7 + 4H^2SO^4 = 2[(Cr^2)'''KS^2O^8] + 4H^2O + O^3.$$

It is also reduced when heated with sulphur or sal-ammoniac. Sulphydric acid precipitates from its solution a mixture of chromic oxide and sulphur. Sulphurous acid colours it green without forming a precipitate, from formation of chromic sulphate and hyposulphate. A solution of the salt in boiling hydrochloric acid deposits on cooling chromo- chloride of potassium (p. 938). The solution of acid chromate absorbs a considerable quantity of nitric oxide, acquiring a dark colour, and depositing after a while brown oxide of chromium.

A concentrated solution of the acid chromate mixed with strong-sulphuric acid, yields a deep red precipitate of chromic acid.

A double salt, composed of *sulphate* and *acid chromate of potassium*, is obtained by mixing a concentrated solution of the acid chromate with a quantity of sulphuric acid less than sufficient to convert the potassium into acid sulphate. It crystallises on cooling in stellate needles. (Reinsch.)

c. *Hyperacid Chromate*, or *Trichromate of Potassium*, $K^2O.3Cr^2O^3$, or $KCrO^2.Cr^2O^3$, separates from a solution of the acid chromate in ordinary nitric acid prepared at 60° C., in dark red nacreous prisms, of specific gravity 3·631, which blacken when exposed to the air, and melt at 145°—150° C. (Graham.)

Chromate of Potassium and Ammonium, $K(NH^4)Cr^2O^4$, crystallises from a concentrated solution of acid chromate of potassium saturated with ammonia, and cooled by a freezing mixture, or evaporated over lime, in crystals apparently isomorphous with sulphate of potassium: when exposed to the air, it gives off ammonia and turns reddish-yellow. (Johnson, J. pr. Chem. lxii. 261.)

Chromate of Potassium with Mercuric Chloride, $KCrO^2.2HgCl$, is obtained by mixing the component salts in equivalent proportions, and adding sufficient hydrochloric acid to redissolve the precipitate first produced. Small slightly reddish crystals, which form a yellow solution in water. Another salt, $2KCrO^2.Cr^2O^3.2HgCl$, is obtained in red spicular crystals, by mixing acid chromate of potassium and mercuric chloride in equivalent proportions, and leaving the solution to evaporate. (Darby, Chem. Soc. Qu. J. i. 24.)

Chromate of Potassium with Mercuric Cyanide, $2KCrO^2.3HgCy$.—Light yellow laminar crystals, obtained by evaporating a solution of 1 pt. neutral chromate of potassium and 3 pts. cyanide of mercury. (Darby.)

Chromo-chloride of Potassium, $KCl.Cr^2O^3 = \left.\begin{matrix}(Cr^2O^2)'' \\ K\end{matrix}\right\}\begin{matrix}O \\ Cl\end{matrix}$. This salt, which is analogous in composition to the triacid chromate $KCrO^2.Cr^2O^3$, is obtained by dissolving together, with aid of heat, 3 pts. acid chromate of potassium, and 4 pts. hydrochloric acid, avoiding evolution of chlorine. It crystallises in flat, red, rectangular prisms, and is decomposed by solution in water.

CHROMATES OF SILVER.—The *neutral salt*, $AgCrO^2$, is obtained as a red precipitate by decomposing neutral chromate of potassium with nitrate of silver, or by boiling the acid silver-salt with water, whereby it is partly resolved into chromic acid and the neutral chromate, which then separates in crystals green by transmitted light, and yielding a red powder. A solution of the acid salt in ammonia deposits the neutral salt on evaporation, in dark green metallic crusts.

Acid Chromate of Silver, $2AgCrO^2.Cr^2O^3$, is obtained by immersing metallic silver in solution of acid chromate of potassium mixed with sulphuric acid, or by precipitating the same acidulated solution with a silver-salt. It has the colour of carmine, is partly soluble in water, and crystallises therefrom in triclinic prisms, having a dark brown colour, red by transmitted light, and yielding a red powder.

Ammonio-chromate of Silver, $2NH^3.AgCrO^2$, separates from a hot solution of chromate of silver in ammonia, in yellow, square prisms, isomorphous with the corresponding salts of sulphuric and selenic acid: they give off ammonia when exposed to the air.

CHROMATES OF SODIUM.—Two of these salts are known, namely, the *neutral chromate*, $NaCrO^2$, and the *acid chromate*, $2NaCrO^2.Cr^2O^3$. They are analogous in all respects to the neutral and acid chromates of potassium, and may be prepared in like manner. The neutral salt, which may also, according to Johnson (J. pr. Chem. lxii. 161), be obtained by saturating a solution of acid chromate of potassium with carbonate of sodium, and leaving it to evaporate at 0° C., crystallises at low temperatures in yellow transparent crystals, containing $NaCrO^2.5aq.$, isomorphous with Glauber salt: they melt at the heat of the hand, deliquesce rapidly in the air, are easily soluble in water, sparingly in alcohol, and when immersed in alcohol, become opaque from loss of water. The aqueous solution evaporated at temperatures above 30° C., deposits the anhydrous salt.

Acid chromate of sodium, $2NaCrO^2.Cr^2O^3$, forms thin, hyacinth-red prisms, very soluble in water.

CHROMATE OF STRONTIUM.—Light yellow powder, obtained by precipitation; soluble in hydrochloric, nitric, and chromic acid; rather more soluble in water than the barium-salt.

CHROMATES OF TIN.—Stannic chloride forms with chromate of potassium a yellow precipitate, which becomes brownish-yellow and translucent when dry, and passes into violet stannic chromate when ignited.

Stannous chromate is precipitated in yellow curdy flocks, when stannous chloride is added with stirring to excess of chromate of potassium. If the contrary course be adopted, a greenish-white precipitate is formed, perhaps consisting of chromic stannate. The salt leaves a violet residue when ignited.

URANIC CHROMATE.—Uranic nitrate forms an ochre-yellow precipitate with neutral chromate of potassium. The yellow rough-tasting solution of uranic carbonate in aqueous chromic acid, yields small fiery-red crystals. The salt melts at a gentle heat, with partial decomposition.

Chromate of Vanadium.—The brownish-yellow solution of vanadic hydrate in aqueous chromic acid, yields on evaporation, a shining, dark brown, varnish-like mass, which dissolves partially in water, forming a yellow liquid.

Chromate of Yttrium.—Soluble salt, crystallising in small yellow prisms.

Chromate of Zinc.—Sulphate of zinc, mixed with neutral chromate of potassium, forms a yellow precipitate of a basic salt. Malaguti and Sarzeau, by treating carbonate of zinc with pure chromic acid, obtained a yellow crystalline basic salt, containing $4Zn^2O.Cr^2O^3 + 5$ aq., or $Zn^2CrO^4.ZnHO + 2$ aq. By boiling this salt with chromic acid as long as anything dissolves, the same chemists obtained a soluble non-crystalline salt, $2Zn^2O.3Cr^2O^3$, or $4ZnCrO^2.Cr^2O^3$.

Ammonio-chromate of Zinc.—The tetrabasic salt repeatedly treated with ammonia, yields yellow cubic crystals, containing $2(ZnCrO^4.NH^3) + 5$ aq. Soluble chromate of zinc, $2Zn^2O.3Cr^2O^3$, treated with excess of ammonia and then with alcohol, yields a copious precipitate, consisting of microscopic needles containing $5NH^3.4ZnCrO^2 + 9$ aq. (Malaguti and Sarzeau.)

Chromate of Zinc and Potassium.—The precipitate formed by chromate of potassium in sulphate of zinc, if left for some time under the liquid, changes to an orange-yellow powder, consisting of the double salt. It is sparingly soluble in cold water, but imparts a yellow colour to a large quantity of the liquid; in boiling water, it dissolves with deep yellow colour, with separation of a lighter coloured basic salt. When ignited, it leaves a dark brown residue, from which water extracts neutral chromate of potassium, leaving a compound of sesquioxide of chromium and oxide of zinc. (Handw. d. Chem. ii. [2] 1246.)

CHROME ALUM. This name is applied to the double sulphates of chromium and the alkali-metals, analogous in composition to common alum and isomorphous therewith, *e.g. potassio-chromic sulphate*, $K(Cr^2)'''(SO^4)^2 + 12H^2O = \left.\begin{matrix}(S^2O^4)^{iv} \\ K.(Cr^2)'''\end{matrix}\right\} O^4 + 12H^2O$.

CHROME GREEN. A name applied sometimes to green oxide of chromium, sometimes to the pigment produced by mixing chrome yellow with Prussian blue. (See Chromate of Lead, p. 934.)

CHROME IRON ORE. *Chromic Iron, Chromate of Iron, Chromeisenstein, Eisenchrom, Ferrochromate.*—This mineral, which is the most abundant ore of chromium, usually occurs massive, with fine granular or compact structure, forming veins or imbedded masses in serpentine; more rarely in regular octahedrons, with imperfect cleavage parallel to the octahedral faces. Specific gravity 4·32 to 4·57. Hardness 5·5. Colour brownish-black, or iron-black. Streak brown. Lustre submetallic, inclining to waxy. Opaque. Brittle, with conchoïdal or uneven fracture. Sometimes magnetic. Before the blowpipe it does not fuse, but becomes more strongly magnetic. With borax or phosphorus-salt it fuses with difficulty, but completely, to a beautiful green globule.

Chrome iron ore belongs to the spinel group of minerals, whose general formula is $M^2O.R^4O^3$ or $\left.\begin{matrix}M' \\ (R^2)'''\end{matrix}\right\} O^2$. The monatomic metal is chiefly iron, but magnesium is generally also present in considerable quantity, and in some specimens a small portion of the chromium appears to exist as chromosum. The sesqui-atomic metal R is principally chromium, but it is replaced to a considerable extent by aluminium, and sometimes also by iron (ferricum), so that the general formula of the mineral is $\left.\begin{matrix}Fe;\ Mg;\ Cr; \\ Cr^2;\ Al^2;\ Fe^2;\end{matrix}\right\} O^2$. From the numerous analyses that have been made of it, we select the following as samples of the different varieties: *a*, from Baltimore, Maryland, by Abich (Pogg. Ann. xxxiii. 335); *b*, from Volterra, Tuscany, by Bechi (Sill. Am. J. [2] xiv. 62); *c*, from Texas, Lancaster county, Pennsylvania, by Franke (*Rammelsberg's Mineralchemie*); *d*, from the same, by Garrett (Sill. Am. J. [2] xiv. 46); *e*, crystallised, from Baltimore, by Abich (*loc. cit.*); *f*, from Beresow, Siberia, by Moberg (J. pr. Chem. xliii. 119):

	a	*b*	*c*	*d*	*e*	*f*
Cr^4O^3 . .	55·37	44·23	55·14	63·38	58·25	59·30
Cr^2O . .	—	—	—	—	1·61	4·39
Fe^4O^3 . .	1·10	0·33	12·06	—	—	—
Fe^2O . .	18·04	35·32	18·02	38·66	20·13	18·59
Al^4O^3 . .	13·97	20·83	5·75	—	11·85	10·93
Mg^2O . .	10·04	—	9·39	—	7·45	6·74
Ni^2O . .	—	—	—	2·28	—	—
	98·52	100·71	100·36	104·32	99·29	100·45

Besides the above localities, chrome-iron ore is found in the islands of Unst and Fetlar in the Shetland group, in the Département du Var in France, in Silesia and Bohemia, at Röraas in Norway, near Kraubat in Syria, abundantly in Asia Minor and the Eastern Urals, and in several parts of North America. It assists in giving the green colour to verd-antique marble. The ore used in this country is obtained chiefly from the Shetland Isles, Norway, and Baltimore, the quantity amounting to 2000 tons annually. (Dana, ii. 106; *Rammelsberg's Mineralchemie*, p. 172.)

CHROME-MICA. This name was given by Breithaupt to an emerald-green mica with nacreous lustre from the Pinzgau.

CHROME-OCHRE. Native chromic oxide.

CHROME-RED and **CHROME-YELLOW.** See CHROMATES OF LEAD (p. 934).

CHROMIC ACID. (pp. 931, 952).—**CHROMITE.** Syn. with CHROME-IRON ORE.

CHROMITES. Compounds of sesquioxide of chromium with protoxides (p. 951).

CHROMIUM. *Symbol* Cr. *Atomic weight* 26·2.—This metal was discovered by Vauquelin in 1797. It is not very abundant, and never occurs in the free state. It is found as sesquioxide (*chrome-ochre*), as sesquioxide combined with protoxide of iron (*chrome-iron ore*), as chromate of lead (*crocoisite* or *red lead-spar*, p. 934); in small quantity in many iron ores, and frequently in meteoric iron; it is also the colouring principle of many minerals, as the emerald, green serpentine, olivin, &c.

The most abundant ore of chromium is chrome-iron. This mineral ignited with alkalis in presence of oxidising agents, yields a chromate of the alkali-metal; these salts treated with acids and reducing agents yield sesquioxide of chromium; and from this substance the metal itself, and many of its compounds, may be prepared.

Metallic chromium is obtained by reduction of the oxides or chlorides, as when sesquioxide of chromium is mixed with one-third of its weight of lamp-black or sugar-charcoal and exposed in a crucible lined with charcoal to the heat of a blast furnace; the metal is thereby obtained as a whitish-grey mass, which cannot be melted together into a button. Péligot, by heating the violet sesquichloride of chromium with potassium, obtained the metal in the form of a dark grey powder. Frémy, by heating the sesquichloride in a porcelain tube and passing vapour of sodium over it in a current of hydrogen, obtained it in very hard shining crystals. Bunsen, by electrolysing a solution of the sesquioxide, obtained the metal in brittle laminæ, having the colour of iron and metallic lustre. According to Berzelius, when sesquichloride of chromium is heated in an atmosphere of hydrogen, there is obtained, besides the protochloride, a shining deposit of metallic chromium.

Wöhler (Ann. Ch. Pharm. cxi. 230) obtains metallic chromium by reducing the sesquichloride with zinc. One pt. of the violet sesquichloride, and 2 pts. of a mixture of the chlorides of potassium and sodium (7 pts. chloride of sodium to 9 pts. chloride of potassium) are closely pressed into an ordinary earthen crucible, 2 pts. of zinc are laid on the mixture, and the whole is covered with a layer of the flux. The crucible is then gradually heated to redness, and the mass is kept in a state of fusion, till a hissing noise is heard, and a zinc-flame is observed on removing the cover for a moment. The crucible is then taken out, gently tapped to cause the metal to collect, and left to cool. A good regulus of zinc is then found at the bottom covered with a green slag. This regulus is well washed with water and digested in dilute nitric acid, which dissolves the zinc, and leaves the chromium in the form of a grey powder, which must be purified by again heating it with nitric acid and washing. By this method Wöhler obtained 6 or 7 grms. of metal from 30 grms. of the chloride, the calculated quantity being 10 grms. Magnesium may be used in the reduction instead of zinc, but it offers no particular advantage. With cadmium as the reducing agent, a violent explosion occurred.

Chromium obtained by Wöhler's process is a light green, glistening, crystalline powder, which, when magnified fifty times, exhibits aggregates of crystals like fir-branches, interspersed with individual crystals of tin-white colour, high lustre, and specific gravity 6·81 according to Wöhler, 7·3 according to Bunsen. These crystals, according to Wöhler, have the form of a very acute rhombohedron; but according to Bolley (Chem. Soc. Qu. J. xiii. 334), who examined them with a magnifying power of 85, they are quadratic octahedrons with acuminated summits and bevelled terminal edges, and very frequently united by fours in the form of a cross. This is the third example known of an elementary body crystallising in the dimetric or quadratic system, the others being tin and boron; as a general rule, ductile metals crystallise in the monometric or regular system; brittle metals in the hexagonal system.

Wöhler's chromium does not exert the slightest action on the magnetic needle. When heated to redness in the air, it acquires a yellow and blue tarnish like steel, and gradually becomes covered with a thin film of green oxide; but the oxidation is by no means complete. Thrown into a spirit flame fed with oxygen, it burns with sparkling, but not so brightly as iron. On melting chlorate of potassium it burns with dazzling white light. Melting nitre oxidises it very readily, but without incandescence. In melting carbonate of sodium it remains unaltered. Heated in chlorine gas, it exhibits vivid incandescence. It is but superficially converted into green oxide by ignition in a stream of aqueous vapour free from air. Hydrochloric acid dissolves it readily, with evolution of hydrogen, forming blue chromous chloride. Dilute sulphuric acid does not act upon it at ordinary temperatures, but on applying a gentle heat, a violent action suddenly takes place, and the remaining metal acquires the power of dissolving easily in the most dilute sulphuric acid, even after washing. It is not attacked by nitric acid, either concentrated or dilute. (Wöhler.)

The properties of chromium differ considerably, according to the manner in which it is prepared, the peculiarity doubtless depending chiefly on the state of aggregation. Péligot's chromium oxidised with great facility, taking fire in the air, even at a heat below redness, and being converted into green sesquioxide. It likewise dissolved in dilute sulphuric and hydrochloric acids, and was oxidised by nitric acid.

The crystals of chromium obtained by Frémy belong, according to Sénarmont, to the regular system. They were not attacked by any acid, not even by nitromuriatic acid.

Chromium may be polished, and then acquires a fine metallic lustre. When pure it is even less fusible than platinum (Deville, Polyt. Centralbl. 1857, p. 605). A fragment of it scratches glass; it is at least as hard as corundum.

Chromium unites with *bromine*, *chlorine*, *fluorine*, *iodine*, *cyanogen*, *nitrogen*, *oxygen*, *phosphorus*, and *sulphur*, also with *aluminium* and *iron*. There are two classes of chromium-compounds, into which the chromium enters as the positive or basic element, namely, the chromous compounds, in which it is monatomic, *e. g.* $CrCl$, Cr^2O, Cr^2SO^4, &c., and the chromic compounds, in which it is sesquiatomic *e. g.* Cr^2Cl^3, Cr^4O^3, $Cr^4(SO^4)^3$, &c. It likewise forms an oxide or anhydride, Cr^2O^3, in which it is triatomic, and to this there corresponds a class of salts, the chromates, into which the chromium likewise enters as a triatomic radicle, *e. g.* chromate of lead, $\left.\begin{matrix}Cr'''\\Pb\end{matrix}\right\}O^2$.

CHROMIUM, BROMIDES OF. The *anhydrous sesquibromide*, Cr^2Br^3, may be prepared, like the chloride, by passing bromine-vapour over an ignited mixture of chromic oxide with charcoal and starch-paste. Part of the resulting bromide then sublimes beyond the mass of oxide, while another portion remains therein in crystalline scales, which, however, are easy to separate. It forms black semi-metallic hexagonal scales, translucent with olive-green colour, and exhibiting in one direction a faint red dichroism. It forms a yellowish-green powder when triturated, in which form also part of the compound sublimes during the preparation. It is quite insoluble when pure, but dissolves to a green liquid if mixed with protobromide. It is decomposed by alkalis more easily than the chloride. When gently heated in hydrogen gas, it is reduced to the white protobromide, $CrBr$, which on exposure to the air quickly deliquesces to green oxybromide. (Wöhler, Ann. Ch. Pharm. lxi. 382.)

A solution of chromic bromide is obtained by dissolving chromic hydrate in hydrobromic acid, or by treating chromate of silver with hydrobromic acid and alcohol. The solution yields green crystals, and is easily decomposed by evaporation, with formation of oxybromide.

CHROMIUM, CHLORIDES OF. Two chlorides of chromium are known in the free state, viz. $CrCl$ and Cr^2Cl^3. A trichloride, $CrCl^3$, may also be supposed to exist, combined with chromic anhydride, in chlorochromic anhydride, $CrCl^3.Cr^2O^3$.

Protochloride of Chromium or Chromous Chloride. $CrCl$. (Moberg, J. pr. Chem. xxix. 175; Péligot, Ann. Ch. Phys. [3] xii. 527.)—This compound is obtained by passing hydrogen gas over perfectly anhydrous sesquichloride of chromium very gently heated, as long as hydrochloric acid gas continues to escape. The hydrogen must be previously freed from all traces of oxygen by passing it through a solution of protochloride of tin in caustic potash, then through tubes containing sulphuric acid and chloride of calcium, and lastly over red-hot metallic copper. The protochloride is also formed by passing dry chlorine gas over a red-hot mixture of charcoal and chromic oxide. The first method yields the protochloride in the form of a white, velvety substance, retaining the form of the sesquichloride from which it has been formed; the second method yields it in fine white crystals, usually mixed, however, with chromic oxide, chromic chloride, and charcoal.

Protochloride of chromium dissolves in water, with evolution of heat, forming a blue solution, which rapidly turns green when exposed to the air or to chlorine gas. With *potash* it forms a dark brown precipitate (yellow, according to Moberg, if the air be completely excluded) of hydrated chromous oxide, which, however, quickly changes to light brown chromosochromic oxide, with evolution of hydrogen. *Ammonia* forms a sky-blue precipitate, which turns green on exposure to the air. With ammonia and sal-ammoniac, a blue liquid is formed, which turns red on exposure to the air. *Sulphide* *of ammonium* or *potassium* forms a black precipitate of chromous sulphide. The solution of protochloride of chromium is one of the most powerful deoxidising agents known. With a solution of *neutral chromate of potassium*, it forms a dark brown precipitate of chromosochromic oxide, which, however, disappears on the addition of an excess of the protochloride, and forms a green solution. It precipitates *calomel* from a solution of corrosive sublimate. With *cupric salts*, it forms at first a white precipitate of cuprous chloride, but when added in excess, throws down red cuprous oxide. It instantly converts *tungstic acid* into blue oxide of tungsten, and precipitates *gold* from the solution of the chloride.

A solution of chromous chloride containing zinc, may be obtained, according to Loewel (J. pr. Chem. lxii. 11), by pouring a solution of the sesquichloride, or of chrome-alum, in 3 to 5 pts. water, made as neutral as possible, into a bottle nearly filled with granulated zinc. Hydrogen is then evolved for some hours, and a fine blue liquid is formed, which, if left to stand in contact with the zinc, continues slowly to evolve hydrogen and deposit a light grey chromous oxychloride, and after four or six months becomes perfectly colourless.

SESQUICHLORIDE OF CHROMIUM. Chromic Chloride. Cr^2Cl^3.—The anhydrous sesquichloride is prepared by igniting an intimate mixture of chromic oxide and charcoal in a stream of dry chlorine gas. A mixture of the oxide with lamp-black is made up into pellets with starch; these are well baked in a covered crucible, and then introduced into another crucible, through the bottom of which there passes a porcelain tube connected with an apparatus for evolving chlorine. Into the mouth of this crucible is fitted a smaller one, placed in an inverted position. The lower crucible stands on the grate of an ordinary air-furnace, and, as soon as the apparatus is filled with dry chlorine, the mixture is heated to bright redness, the firing being so regulated as to keep the upper crucible comparatively cool, so that the chloride as it is produced may sublime into it. When the process is completed, the stream of chlorine must be kept up till the apparatus is cool, to prevent the formation of sesquioxide or protochloride. The sesquichloride is then washed with water to free it from chloride of aluminium derived from the crucible. If it contains protochloride, which is the case if the stream of chlorine has not been strong enough, it will dissolve during washing (Wöhler, Pogg. Ann. xi. 148). The sesquichloride may also be obtained by heating the sesquisulphide in a stream of dry chlorine. (Berzelius.)

Anhydrous chromic chloride forms shining micaceous laminæ of a beautiful peach-blossom colour, which may be rubbed on the skin like talc. It is quite insoluble in cold water; but, if boiled in the finely divided state with water, it slowly dissolves and forms a green solution. If the cold water contains in solution a small quantity of chromous chloride, not even exceeding $\frac{1}{4000}$ to $\frac{1}{1000}$, the sesquichloride dissolves immediately, with evolution of heat, forming a green solution identical with that obtained by dissolving chromic hydrate in hydrochloric acid. This effect is perhaps due to the formation of an intermediate chloride, which is immediately resolved by the action of water into protochloride and the soluble green modification of the sesquichloride, the protochloride thus liberated again acting in the same manner (see p. 943). The addition of a small quantity of stannous or cuprous chloride is said to produce the same effect.

Anhydrous chromic chloride is not decomposed by sulphuric acid, either strong or dilute, or by hydrochloric, nitric, or nitromuriatic acid, or by ammonia, carbonate of potassium, or carbonate of sodium: *caustic potash* attacks it but slightly at the boiling heat. Fused with *nitre* and an *alkali* or *alkaline carbonate*, it yields a chromate and chloride of the alkali-metal. *Potassium, zinc*, &c., separate metallic chromium from it. Heated in a stream of *hydrogen*, it yields chromous chloride, and if the heat be strong, metallic chromium is likewise separated. Heated to redness in the *air*, it gives off chlorine and yields green chromic oxide. By ignition in *phosphoretted hydrogen gas*, it is converted into phosphide of chromium. Heated with *sulphur*, or in a stream of *sulphydric acid gas*, it yields sulphide of chromium. Ignited in *ammonia gas*, it forms nitride of chromium.

By dissolving chromic oxide in hydrochloric acid, or by boiling chromate of lead or silver with hydrochloric acid and alcohol, or even with excess of hydrochloric acid alone, a green solution is obtained, containing the modification of chromic chloride which corresponds to the green chromic oxy-salts (p. 950). This solution, when evaporated, yields a non-crystalline dark green syrup, which, when heated to 100° C. in a stream of dry air, yields a green mass containing $2Cr^2Cl^3.9H^2O$ (Moberg, J. pr. Chem. xxix. 175). The same solution evaporated in vacuo yields green granular crystals containing $Cr^2Cl^3.H^2O$. (Péligot, *ibid.* xxxvii. 475.)

Hydrated chromic chloride heated to 250° C. in a stream of hydrochloric acid or chlorine gas, gives off its water and yields delicate peachblossom-coloured scales, which are soluble in water and even deliquescent; but, if more strongly heated in either of these gases, it begins to sublime, and the sublimed chloride thus obtained is insoluble in water, like that obtained by igniting chromic oxide with charcoal in a stream of chlorine. The anhydrous chloride cannot be obtained by heating the hydrated chloride in the air: for hydrochloric acid is then given off and soluble oxychloride produced, afterwards an insoluble oxychloride, and the residue ultimately consists of green chromic oxide. In this respect, the hydrated sesquichloride of chromium resembles the corresponding compounds of iron and aluminium.

Nitrate of silver added to a green solution of chromic chloride, throws down at first only $\frac{1}{3}$ of the chlorine; but on leaving the liquid to stand, or on boiling it, the whole of the chlorine is precipitated. This effect was attributed by Berzelius to the tendency of chromic chloride to form double salts; by Otto to the solubility of chloride of silver in chromic nitrate.

A solution of chromic chloride, corresponding to the violet solutions of the chromic salts of oxygen-acids, may be obtained by precipitating one of these violet salts by an alkali, and dissolving the precipitated hydrate in hydrochloric acid; also by decomposing the violet sulphate with chloride of barium. From these solutions nitrate of silver immediately throws down all the chlorine. If, however, the violet solution of the chloride be boiled, it turns green, and after this change the chlorine is but partially precipitated by nitrate of silver.

Chromic chloride unites with the chlorides of the more basic metals, forming salts containing $MCl.Cr^2Cl^3$, or MCr^2Cl^4, of which however only the potassium, sodium, and ammonium-compounds have been investigated. They are obtained by mixing the corresponding acid chromates with excess of hydrochloric acid and alcohol, and evaporating over the water-bath till the mass turns violet. The double chlorides thus obtained become green and deliquesce on exposure to the air. Treated with a small quantity of cold water, they dissolve, with deep yellowish-red colour, which in a short time passes into pure chrome-green. If the solution be then left to evaporate, the alkaline chloride separates out, and the chromic chloride remains in the form of a green syrup. These double chlorides belong therefore to the violet modifications of chromic salts, but are decomposed by water into chloride of alkali-metal and green chromic chloride, which does not form double chlorides. The effect of chromous, stannous, and cuprous chlorides in facilitating the solution of anhydrous chromic chloride in water (p. 942) probably depends upon the formation of analogous double chlorides. If the double chloride decomposed by slow evaporation be mixed with hydrochloric acid and evaporated to dryness over the water-bath, the double chloride is reproduced. When the dry double chlorides are treated with absolute alcohol, green chromic chloride dissolves, and a rose-coloured salt remains, consisting, according to Berzelius, of $3MCl.Cr^2Cl^3$.

CHROMIUM, DETECTION AND ESTIMATION OF. 1. All compounds of chromium ignited with a mixture of *nitre* and an *alkaline carbonate* yield a chromate of the alkali-metal, which may be dissolved out by water, and on being neutralised with acetic acid, will give the characteristic precipitates of chromic acid with lead and silver-salts.

The oxides of chromium and their salts, fused with *borax* in either blowpipe flame, yield an emerald-green glass. The same character is exhibited by those salts of chromic acid whose bases do not of themselves impart decided colours to the bead. The production of the green bead in both flames distinguishes chromium from uranium and vanadium, which give green beads in the inner flame only.

2. *Reactions in Solution.*—The sesqui-salts of chromium or chromic salts exhibit two principal modifications, the green and the violet. *Ammonia* produces in solutions of the green salts, a greyish-green precipitate; in solutions of the violet salts, a greyish-blue precipitate, both of which however yield green solutions with sulphuric or hydrochloric acid. The liquid above the precipitate has a reddish colour, and contains a small quantity of chromic acid. *Potash* and *soda* form similar precipitates, which dissolve in excess of the alkali, forming green solutions from which the chromic oxide is precipitated by boiling. The *alkaline carbonates* form greenish precipitates (violet by candle-light) which dissolve to a considerable extent in excess of the reagent. *Sulphydric acid* forms no precipitate; *sulphide of ammonium* throws down the hydrated sesquioxide.

Zinc, immersed in a solution of chrome-alum or sesquichloride of chromium, excluded from the air, gradually reduces the chromic salt to a chromous salt, the liquid after a few hours acquiring a fine blue colour, and hydrogen being evolved by decomposition of water. If the zinc be left in the liquid after the change of colour from green to blue is complete, hydrogen continues to escape slowly, and the liquid, after some weeks or months, is found no longer to contain chromium, the whole of that metal being precipitated in the form of a basic salt, and its place taken by zinc. *Tin*, at a boiling heat, likewise reduces the chromic salt to a chromous salt, but only to a limited extent;

and on leaving the liquid to cool after the action has ceased, a contrary action takes place, the protochloride of chromium decomposing the protochloride of tin previously formed, reducing the tin to the metallic state, and being itself reconverted into sesquichloride. *Iron* does not reduce chromic salts to chromous salts, but merely precipitates a basic sulphate of chromic oxide, or an oxychloride, as the case may be.

Chromous salts are but rarely met with in solution: for their characters, see Protochloride of Chromium (p. 942).

Chromic acid and its salts are recognised in solution by forming a pale yellow precipitate with *barium*-salts, bright yellow with *lead*-salts, brick red with *mercurous*-salts, and crimson with *silver*-salts (p. 932).

3. *Quantitative Estimation.*—Chromium is usually estimated in the state of sesquioxide. When it exists in solution as a sesqui-salt, it may be precipitated by ammonia, care being taken to avoid a large excess of that reagent (which would dissolve a portion), and to heat the liquid for some time. The chromic oxide is then completely precipitated, and the precipitate, after washing and drying, is reduced by ignition to the state of anhydrous sesquioxide, containing 69·1 per cent. of the metal.

When chromium exists in solution in the state of chromic acid, it is best to precipitate it by a solution of mercurous nitrate; the mercurous chromate thereby thrown down yields by ignition the anhydrous sesquioxide. The chromic acid might also be precipitated and estimated in the form of a barium or lead-salt.

Chromic acid may also be estimated by means of oxalic acid, which reduces it to sesquioxide, being itself converted into carbonic acid. The quantity of carbonic anhydride evolved determines the quantity of anhydrous chromic acid present, 3 at. CO^2 corresponding to 1 at. Cr^2O^3, as shown by the equation:

$$2Cr^2O^3 + 3C^2H^2O^4 = Cr^4O^3 + 6CO^2 + 3H^2O.$$

The mixture may be heated in the carbonic acid flask represented in *fig.* 5, p. 119. If the object be merely to determine the quantity of chromium present, any salt of oxalic acid may be used; but if the alkalis are also to be estimated in the remaining liquid, the ammonium or barium-salt must be used.

Lastly, chromic acid may be estimated by Bunsen's volumetric method. The chromic acid is decomposed by boiling with excess of hydrochloric acid, whereupon 1 at. chromic anhydride eliminates 3 at. chlorine:

$$Cr^2O^3 + 6HCl = Cr^2Cl^3 + 3H^2O + Cl^3;$$

and the 3 at. chlorine passed into a solution of iodide of potassium, liberate 3 at. iodine, which is estimated by a standard solution of sulphurous acid, as described under Volumetric Analysis (p. 264), so that 3 at. iodine correspond to 1 at. Cr^2O^3.

4. *Separation of Chromium from other Elements.*—Chromic oxide, in the state of neutral or acid solution, is easily separated from the *alkalis* or *alkaline earths* by precipitation with ammonia, care being taken in the latter case to protect the liquid and precipitate from the air. The same method, with addition of sal-ammoniac, serves to separate chromic oxide from *magnesia*. The separation from the alkaline earths and from magnesia may also be effected by precipitating the whole with an alkaline carbonate, and igniting the precipitate with a mixture of carbonate of sodium and nitre. The chromium is then converted into chromate of sodium, which may be dissolved out, and the solution, after neutralisation with nitric or acetic acid, treated with mercurous nitrate as above.

From *alumina* and *glucina*, chromic oxide may be separated by treating the solution with excess of potash, and boiling the liquid to precipitate the chromic oxide. The separation is, however, more completely effected by fusing with nitre and carbonate of sodium, treating the fused mass with water, adding an excess of nitric acid to dissolve anything that may be insoluble in water, and precipitating the alumina or glucina by ammonia.

Another method of converting chromic oxide into chromic acid, and thereby effecting its separation from the above-mentioned oxides, is to treat the mixture with excess of potash, and heat the solution gently with peroxide of lead. The whole of the chromium is then converted into chromic acid, and remains dissolved as chromate of lead in the alkaline liquid; and on filtering from the excess of peroxide of lead, and any other insoluble matter that may be present, and supersaturating the filtrate with acetic acid, the chromate of lead is precipitated. (Chancel, Compt. rend. xliii. 927.)

Chromic acid may be separated from the *alkalis* in neutral solutions by precipitation with mercurous nitrate; also by reducing it to chromic oxide with hydrochloric acid and alcohol, and precipitating by ammonia. From the *earths* it may also be separated by this latter method, or, again, by fusing with carbonate of sodium, dissolving out with water, &c.

From *iron*, *zinc*, *nickel*, *cobalt*, *uranium*, and *cerium*, chromium may be separated by fusion with nitre and carbonate of sodium, or with the carbonate alone if it is already in the form of chromic acid. Or, again, the separation may be effected by means of potash and peroxide of lead, according to Chancel's method above described.

The separation of chromium from *manganese* cannot be effected immediately in this manner, because the manganese is at the same time converted into manganate or permanganate of sodium; but on dissolving in water and adding alcohol to the solution, the manganese is reduced to peroxide and completely precipitated, while the chromium remains dissolved as chromate.

From *titanium*, *tantalum*, and *columbium*, chromium, if in the state of sesquioxide, may be separated by fusing the mixture with nitre and alkaline carbonate, extracting with water, reducing the chromium to the state of sesquioxide by boiling with hydrochloric acid, and precipitating by ammonia.

From *copper*, *lead*, *tin*, and the other metals of the first group (p. 217), chromium is separated by sulphydric acid.

To estimate chromic acid in presence of *sulphuric acid*, the chromium is first reduced to sesquioxide as above; the sulphuric acid is then precipitated, after considerable dilution, by chloride of barium; the excess of barium is removed by sulphuric acid: and the chromic oxide precipitated by ammonia.

When *phosphoric acid* is present in solution, together with chromic acid, the phosphoric acid is precipitated as phosphate of magnesium and ammonium, and then the chromic acid by any of the preceding methods.

Hydrochloric acid is separated from chromic acid by nitrate of silver, and the excess of silver is removed by sulphuretted hydrogen, the chromic acid being at the same time reduced to sesquioxide, which may be precipitated by ammonia.

Silicic acid is separated from chromic acid in the same manner as from all other substances, and the chromium is afterwards precipitated as oxide.

When sesquioxide of chromium and chromic acid occur together in solution, the chromic acid may be precipitated by mercurous nitrate, the solution being first completely neutralised, and the sesquioxide precipitated from the filtrate by ammonia, which at the same time throws down a mercury-compound, to be afterwards separated from the chromic acid by ignition.

Valuation of Chrome-ores.—The value of a chrome-ore depends upon the quantity of chromic acid that it will yield. To ascertain this point, the ore is calcined with a mixture of nitre, alkali, and lime, the use of the lime being to keep the mixture in a pasty condition, and prevent the heavy ore from falling to the bottom (see p. 936), after which the soluble chromate is extracted, and the amount of chromic acid may then be determined by any of the methods already given.

Professor Calvert of Manchester, has given two processes for the valuation of chrome ores. (Chem. Soc. Qu. J. v. 194.)

a. The ore in fine powder is mixed with three or four times its weight of soda-lime (obtained by slaking quick lime with caustic soda, then drying and calcining the mass), and to this mixture of soda-lime and ore is added one-fourth of nitrate of sodium. The whole is then well calcined for two hours, care being taken to stir the pasty mass every quarter of an hour with a platinum wire. This mixture not becoming fluid, the ore is constantly kept in contact with the oxygen of the atmosphere, and thus the oxide of chromium is converted into chromic acid. One treatment is generally sufficient for the complete decomposition of the ore.

The greater part of the mass is now dissolved in water, and the insoluble portion treated with sulphuric acid diluted with twice its bulk of water; the whole is then removed from the crucible, and a little alcohol is added to the solution in order to render the sulphate of calcium insoluble. The whole is next thrown on a filter and washed with weak alcohol, which dissolves all the acid chromate formed, and leaves the sulphate of calcium, together with any portion of ore that may not have been attacked. The sulphate of calcium may be removed by washing the filter with boiling water, and the residual ore, if any, is to be recalcined.

The solution containing the acid chromate of sodium is now neutralised with ammonia, and oxalate of ammonium is added, which gives rise to a small precipitate of sesquioxide of iron, alumina, and oxalate of calcium, together with a little silica dissolved by the sulphuric acid. The precipitate having been separated and well washed, the liquor is either mixed with alcohol to reduce the chromic acid to the state of sesquioxide, which may then be precipitated, washed, dried, ignited, and weighed; or, better, the liquor is rendered acid, and the amount of chromic acid estimated by Penny's process (Chem. Soc. Qu. J. iv. 239) with dichloride* of tin (commonly called *protochloride*). This method depends on the reaction of dichloride of tin with acid chromate of sodium or potassium in presence of free hydrochloric acid, whereby

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* Atomic weight of tin = 118.

the dichloride of tin is converted into tetrachloride, and the chromic acid into sesquichloride of chromium:

$$3SnCl^2 + 2NaCrO^2.Cr^2O^3 + 14HCl = 3SnCl^4 + 2NaCl + 7H^2O + 2Cr^2Cl^6.$$

A solution of dichloride of tin of known strength* is added to the solution of acid chromate of sodium, till the latter is completely decomposed,—which may be known by the solution no longer giving a yellow precipitate with acetate of lead—and the quantity of acid chromate present is calculated from the amount of tin in the solution used. Penny has shown, by direct experiment, that in the above reaction, 100 pts. of metallic tin correspond to 83·2 pts. of acid chromate of potassium, or 78·4 pts. of acid chromate of sodium.

b. The finely divided ore is calcined with nitrate of barium, a small quantity of caustic potash being added towards the end of the operation to facilitate the action, and give rise to chromate of potassium. The pasty condition of the fused baryta prevents the ore from falling to the bottom, and thus keeps it in contact with the air. On cooling, the crucible and its contents are immersed in dilute nitric acid, which dissolves the greater portion of the mass, leaving the unattacked ore, which, after being washed, may be recalcined. The liquor containing the acid chromates of potassium and barium, nitrate of barium, sesquioxide of iron, alumina, and lime, is first heated with sulphate of potassium, which throws down the baryta as sulphate, which is collected on a filter and washed; ammonia and oxalate of ammonium are then added to throw down sesquioxide of iron, alumina, and lime; the mixed precipitate is collected and washed; and the amount of chromic acid determined as before.

5. *Atomic Weight of Chromium.*—Berzelius, in 1818 (Schw. J. xxii. 53), estimated the atomic weight of chromium from the composition of chromate of lead. 100 pts. nitrate of lead (containing 67·31 Pb^2O), yielded by precipitation with chromate of potassium, 98·772 pts. $Pb^2O.Cr^2O^3$; whence, taking the atomic weight of lead at 103·59, that of chromium was found to be 28·14.

Péligot, in 1844 (Ann. Ch. Phys. [3] xii. 528), showed that this number was too high. From the analysis of chromous chloride, CrCl, in which he found 56·7 to 58·4 per cent. chlorine, and likewise from that of the acetate, he estimated the atomic weight of chromium at 26·24.

Berlin (Ann. Ch. Pharm. lvi. 207; lx. 182), analysed chromate of silver by precipitating the silver with hydrochloric acid, then reducing the chromic acid in the filtrate to chromic oxide, and precipitating by ammonia. From the quantity of chloride of silver obtained (Ag = 108; Cl = 35·206), he found, as a mean of five experiments, Cr = 26·34, and by comparing the quantity of chromic oxide precipitated with the original quantity of chromate of silver, Cr = 26·27.

Berlin likewise adopted the method of Berzelius, and found that 100 pts. nitrate of lead yield from 97·559 to 97·594 pts. chromate of lead, whence, as a mean result, Cr = 25·99.

Moberg, in 1841 (J. pr. Chem. xliii. 114; xliv. 322), estimated the atomic weight of chromium by the analysis of chromic sulphate and of ammoniacal chrome-alum. From the quantity of chromic oxide in the sulphate dried at 300° C. he found Cr = 26·55; from that which remained after heating ammonio-chrome-alum to bright redness, Cr = 26·78.

Lefort, in 1850 (J. Pharm. [3] xviii. 27), determined the quantity of baryta in chromate of barium, by dissolving the salt in nitric acid and precipitating by sulphuric acid. In fourteen experiments, he found that 100 pts. chromate of barium yielded 60·35 to 60·01 baryta; mean 60·19: whence, if Ba = 68·56, Cr = 26·64.

Lastly, **Wildenstein**, in 1853 (J. pr. Chem. lix. 27), determined the quantity of chromate of barium precipitated from chloride of barium by neutral chromate of potassium. As a mean of 32 experiments, he found that 100 pts. chromate of barium correspond to 81·70 of the chloride; the limits were 81·52 and 81·86. If then Ba = 68·56 and Cl = 35·46, the value of Cr is 26·76

As the precipitation of baryta by sulphuric acid is affected by an error arising from the carrying down of a portion of the dissolved salt with the precipitated sulphate, and as moreover the atomic weight of barium is not very exactly known, it is probable that the determinations of the atomic weight of chromium by Berlin and by Péligot, are the most exact, and the number 26·24 may be considered very near to the true value. (Handw. d. Chem. 2te Aufl. ii. [1] 482.)

CHROMIUM, FLUORIDES OF. The *sesquifluoride*, Cr^2F^6, is obtained by treating the sesquioxide, dried, but not ignited, with excess of hydrofluoric acid, and heating the dried mass very strongly in a platinum crucible. It is dark green, melts at a high temperature, and is but very slightly volatile, even at the melting point of steel. When subjected to the highest temperature produced by a lamp urged

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* The strength of a solution of dichloride of tin is most easily ascertained by means of a standard solution of pure acid chromate of potassium.

by bellows, it sublimes in shining regular octahedrons (Deville, Ann. Ch. Pharm. cl. 197). Berzelius obtained it as a green crystalline saline mass.

Chromic fluoride unites with the fluorides of ammonium, potassium, and sodium, forming green sparingly soluble compounds.

Trifluoride, CrF^3.—This compound, discovered by Unverdorben, is obtained by distilling 1 pt. of chromate of lead with 1 pt. fluor spar and 3 pts. fuming oil of vitriol in a leaden retort, and collecting the vapours in a perfectly dry leaden receiver kept at a very low temperature: it then condenses to a blood-red, strongly fuming liquid, which becomes gaseous again at a temperature very little higher. The vapour is red, and when inhaled, produces violent coughing and severe oppression of the lungs. It is decomposed by water, forming hydrofluoric and chromic acids, and when it mixes with the air, forms a thick white fume, coloured orange-yellow on the edges by minute particles of chromic acid. With ammonia it unites, according to Unverdorben, forming a yellow volatile body; but, according to Berzelius, it is decomposed with slight explosion, producing nitrogen gas, water, and hydrofluoric acid. Metals and other reducing agents, organic as well as inorganic, abstract part of the fluorine, leaving the sesquifluoride. Silicic acid decomposes it immediately, forming fluoride of silicium and chromic acid; hence it corrodes glass; it may be kept, however, for a while in glass vessels coated with resin.

H. Rose (Pogg. Ann. xxvii. 565), supposed that the formula of this compound was CrF^5, because it contains more fluorine than the formula CrF^3 requires, and its decomposition by water is attended with evolution of oxygen, as well as the formation of chromic and hydrofluoric acids. Berzelius, on the contrary, was of opinion that the excess of fluorine above 3 atoms arose from admixture of hydrofluoric acid, and that the evolution of oxygen in its decomposition by water, was due to the previous mixture of that gas with the vapour of the fluoride, inasmuch as the residue obtained in the preparation of the compound always contains chromic oxide.

A fluoride of intermediate composition between the sesqui- and tri-fluorides is obtained in solution by dissolving brown oxide of chromium in hydrofluoric acid. The solution is red, and yields by evaporation a rose-coloured salt, which is redissolved without alteration by water, and precipitated brown by ammonia.

CHROMIUM, IODIDES OF. The *sesqui-iodide*, Cr^2I^3, is obtained in solution by dissolving chromic hydrate in hydriodic acid, or by treating chromate of silver with hydriodic acid and alcohol. It is green, and yields by evaporation a green glassy residue, which splits into small pieces on cooling. It is insoluble in cold, easily soluble in warm water, but does not separate out again on cooling. No other iodide of chromium is known with certainty.

CHROMIUM, NITRIDE OF. Cr^3N^2? This compound is produced when sesquichloride of chromium is heated in a stream of ammonia-gas: probably thus:

$$3Cr^2Cl^3 + 13NH^3 = 2Cr^3N^2 + 9NH^4Cl + H^3;$$

also when chlorochromic anhydride is treated in a similar manner. It is a brown powder, which, when heated to 150°—200° C. in a stream of oxygen, takes fire and burns with a red light, giving off nitrogen gas and a small quantity of pernitric oxide, and leaving sesquichloride of chromium. (Liebig, Pogg. Ann. xxi. 359.—Schrötter, Ann. Ch. Pharm. xxxvii. 148.—Gm. iv. 139.)

CHROMIUM, OXIDES OF. Chromium forms several compounds with oxygen, namely, the *protoxide*, Cr^2O, the *sesquioxide*, Cr^4O^3, the *trioxide*, or *chromic anhydride*, Cr^2O^3; also an oxide, Cr^3O^2, intermediate between Cr^2O and Cr^4O^3, and several oxides intermediate between Cr^4O^3 and Cr^2O^3.

PROTOXIDE OF CHROMIUM. CHROMOUS OXIDE, Cr^2O. (Moberg, J. pr. Chem. xliv. 322.—Péligot, Ann. Ph. Phys. [3] xii. 528.)—This oxide probably exists in some specimens of chrome-iron ore (p. 939) and in pyrope. It is precipitated as a hydrate by the action of potash on a solution of the protochloride. The anhydrous protoxide has not been obtained. The hydrate, $2Cr^2O.H^2O$, is very unstable, decomposes water even at ordinary temperatures, and unless carefully protected from the air, by precipitating with a well-boiled solution of potash, is converted, as soon as it is formed, into chromoso-chromic oxide, with evolution of hydrogen. It must be dried in an atmosphere of hydrogen. It is yellow when recently precipitated, brown when dry, and may be preserved unaltered in dry air. When ignited, it gives off hydrogen and leaves sesquioxide: $2Cr^2O.H^2O = Cr^4O^3 + H^2$.

Chromous hydrate is insoluble in dilute acids, but dissolves slowly in strong acids. The chromous salts are most easily prepared by mixing a solution of the protochloride with the potassium or sodium-salt of the corresponding acid. They are generally of a red colour, sometimes inclining to blue, dissolve but sparingly in cold water, more readily in hot water. Like ferrous salts, they dissolve large quantities of nitric oxide, forming dark brown solutions. (For their other reactions, see PROTOCHLORIDE OF CHROMIUM, p. 942.)

CHROMOSO-CHROMIC OXIDE, Cr^3O^2, or $Cr^2O.Cr^4O^3$.—Formed when protochloride of chromium is precipitated by potash without the precautions above mentioned for excluding the air. After washing in water and drying in the air, it has the colour of Spanish tobacco. It is but slightly attacked by acids.

SESQUIOXIDE OF CHROMIUM. CHROMIC OXIDE, Cr^4O^3.—This oxide exists in chrome-iron ore (p. 939), and in chrome-ochre. The latter occurs as a yellowish-green, earthy or argillaceous deposit generally mixed with clay, in the Shetland Isles, at Creuzot in France, at Halle and Waldenburg in Silesia, at Martenberg in Sweden, &c. (Dana, ii. 339). It is produced by heating chromium to redness in the air, by the ignition of chromic hydrate, by the decomposition of chromic anhydride and of various chromates, some of these processes yielding it in the amorphous, others in the crystalline state.

a. Amorphous. 1. When mercurous chromate is heated as long as oxygen and vapour of mercury are evolved, chromic oxide remains of a very fine green colour. It is best to heat the salt in a covered crucible, since, if the air has free access to it, part of the sesquioxide is converted into brown oxide, which impairs its colour. (Otto.) —2. When acid chromate of potassium is heated to redness with sulphur, the chromic acid is reduced, sulphurous anhydride is evolved, and there remains a mixture of chromic oxide with sulphide and sulphate of potassium, from which the soluble salts may be extracted by water. (Lassaigne, Ann. Ch. Phys. [3] xiv. 299.)—3. Berthier ignites chromate of potassium in a charcoal crucible, or mixes it with charcoal powder or lamp-black, and ignites it in an ordinary earthen crucible; dissolves the chromite of potassium produced in cold water; heats the filtrate to the boiling point; collects the precipitated hydrate on a filter; washes it thoroughly with water; and lastly ignites it. —4. Wöhler (Pogg. Ann. x. 46) ignites a mixture of acid chromate of potassium with about its own weight of sal-ammoniac and a small quantity of carbonate of sodium in a covered crucible, till no more vapour of sal-ammoniac is disengaged; and then purifies the sesquioxide of chromium from chlorides of potassium and sodium, by washing with water.—5. Barian (Rev. scient. xx. 425) mixes 4 pts. of acid chromate of potassium with 1 pt. of starch; ignites the mixture in a crucible; washes away the resulting carbonate of potassium with water; and again ignites the residue. He states that the chromic oxide thus obtained is so pure that it may be used for glazing porcelain.—6. When acid chromate of ammonium is heated in a platinum or porcelain basin over a lamp, a very energetic action takes place, accompanied by strong incandescence, and green bulky masses of chromic oxide shoot out in every direction, very much resembling unopened tea-leaves. (Böttger, Ann. Ch. Pharm. xlvii. 332.) —7. A very fine and intimate mixture is made of 48 pts. of gunpowder, 240 pts. of perfectly dry acid chromate of potassium, and 5 pts. of equally dry chloride of ammonium. This mixture is made into the shape of a cone (by pressing it into a wine glass, and afterwards carefully shaking it out) and then transferred to an iron plate. A burning fusee or other combustible is then applied to the top of the cone, whereupon it takes fire, and slowly burns throughout its whole mass. On exhausting the cone, while still hot, with water, a residue of chromic oxide is obtained in the form of a pale green powder. (Böttger, *loc. cit.*)

b. Crystallised. 1. When vapour of chloro-chromic anhydride is slowly passed through a glass tube heated to low redness, chlorine and oxygen are evolved, and chromic oxide remains in the tube as a crystalline deposit, sometimes interspersed with larger crystals (Wöhler, Ann. Ch. Pharm. lx. 203).—2. When acid chromate of potassium is heated to whiteness for eighteen hours, a mixture of the neutral chromate and chromic oxide is obtained; and on dissolving out the former with water, chromic oxide remains in fine iridescent spangles (Gentele, J. p. Chem. liv. 184).—3. When dry chlorine is passed over chromate of potassium heated to redness in a porcelain tube, the gas is completely absorbed, oxygen is evolved, and chloride of potassium is formed, together with chromic oxide, in long, shining, green, brittle tablets, if the tube is heated only to a dull redness, but in hard brown crystals like those obtained by Wöhler's method, if the temperature is raised to bright redness (Frémy, Ann. Ch. Pharm. xlix. 274). Blake (*ibid.* cii. 331) found chromic oxide crystallised in plates having the metallic lustre and belonging to the hexagonal system, in the cracks of a furnace which had been used for a long time for the preparation of chromate of potassium from chrome-iron ore.

Crystallised chromic oxide prepared by Wöhler's method forms crystals of rhombohedral character, greenish-black with metallic lustre, and as hard as corundum, so that they scratch glass. Their specific gravity is 5·21, and they yield a greenish powder by trituration.

Amorphous chromic oxide obtained by decomposing the hydrate at a temperature below redness, has a dark green colour; that which has been strongly ignited (methods

1 to 7 p. 948) is bright green. When the oxide prepared at a moderate heat is gradually raised to a higher temperature, it suddenly becomes incandescent and is afterwards nearly insoluble in acids. According to Berzelius, it then contains the indifferent modification of chromium (p. 941). By ignition with nitrate or acid sulphate of potassium, it may be brought back to the soluble state.

Amorphous chromic oxide melts at the heat of a forge-fire, and on cooling forms a greenish-black crystalline mass, exhibiting all the properties of the crystalline oxide obtained by Wöhler's method. It is not reduced by hydrogen gas. Charcoal reduces it at an intense white heat, but only at the points where it is in contact with the charcoal.

Chromic oxide is used in the preparation of green glass and enamel, but especially in the painting of porcelain. It is also used in ordinary painting, forming one of the most permanent greens, called chrome-green.

Hydrated Chromic Oxide. Chromic Hydrates.—Chromic oxide forms several hydrates differing in their properties. When a solution of a green or violet chromic salt is mixed with potash or soda, a bluish-green hydrate is precipitated, which dissolves with emerald-green colour in excess of the precipitant, but is reprecipitated completely as green hydrate on boiling. With ammonia, the violet salts give a grey-blue, the green salts a grey-green precipitate. Both these precipitates dissolve in cold acids, the former with red, the latter with green colour. In excess of ammonia, they both dissolve slowly with peach-blossom colour, the greyish-blue precipitate, however, the more abundantly of the two.

The properties of the hydrates, precipitated by ammonia, are affected to a considerable extent by the concentration and temperature of the chromic solution and of the ammonia, by the way in which they are mixed, &c.; and the results obtained by different experimenters regarding the constitution and properties of these hydrates are by no means accordant. L. Schaffner (Ann. Ch. Pharm. li. 168) describes three modifications of chromic hydrate: the first obtained by boiling chromic chloride with excess of potash, and containing, according to Ordway (Sill. Am. J. [2] xxvi. 197), $Cr^4O^3.4H^2O$, or $H^8Cr^4O^7$; the second, by treating the chloride with sufficient potash to redissolve the precipitate first formed, and neutralising the excess of alkali with hydrochloric acid; the third, by precipitating a solution of a chromic salt with excess of ammonia: the dried precipitate thus obtained is, according to Schaffner, $Cr^4O^3.6H^2O$, or $H^{12}Cr^4O^9$.

The following results have been obtained by Lefort (J. Pharm. [3] xviii. 27). When a chromic salt is treated with excess of caustic soda-solution, the precipitate first formed redissolves with green colour if the original chromic salt was green or red, with bluish-violet colour if the chromic salt was bluish-violet. The solutions, if heated, deposit a gelatinous hydrate of fine green colour, containing $Cr^4O^3.5H^2O$, or $H^5Cr^2O^4$. It becomes hard and black when dry, and yields a dark green powder. The same hydrate is obtained by pouring a chromic salt of either modification into excess of the boiling alkali-solution.

Another green hydrate, $Cr^4O^3.6H^2O$, or $H^{12}Cr^4O^9$, is deposited when the solution of chromic oxide in excess of alkali is left to itself. It exhibits the same properties as the preceding (Lefort). According to Frémy, these hydrates contain 8 and 9 aq. respectively.

A hydrate containing $Cr^4O^3.7H^2O$, or $H^7Cr^2O^5$, is obtained when a solution of violet chrome-alum is poured into excess of ammonia; the precipitated oxide then turns red and redissolves, and, on heating the ammoniacal solution to a temperature not exceeding 50° C., a greyish-green pulverulent precipitate is formed, having the composition just stated, and dissolving in acids with violet colour. (Lefort.)

d. $Cr^4O^3.9H^2O$, or $H^9Cr^2O^6$.—This hydrate is deposited as a violet powder when the ammoniacal-solution of chrome-alum is left to evaporate in the air or over oil of vitriol. When dry, it forms a greyish-violet, very light powder; when dissolved in acids, it yields red salts. (Lefort.)

According to Frémy, this hydrate is obtained by precipitating a violet chromic salt with ammonia, and drying the precipitate in vacuo. It dissolves in acetic acid, ammonia, and dilute potash-ley. Its properties are liable to considerable alteration from apparently trifling circumstances; thus, by the action of boiling water, or by prolonged contact with cold water, by the action of concentrated saline solutions, by desiccation for several days in the air or in vacuo, and trituration, it is rendered insoluble in liquids in which it was previously soluble. Frémy is of opinion that these alterations result from an allotropic modification of the chromic oxide, and not from loss of water. He applies the term chromic oxide to the oxide which has been rendered insoluble in acetic acid, potash, and ammonia in the manner just mentioned, and metachromic oxide to that oxide which is soluble in these reagents, and is precipitated by ammonia from a violet chromic salt.

A chromic hydrate, much used as a pigment, is the **emerald-green** of Pannetier, $Cr^4O^3.2H^2O = H^4Cr^4O^6$. It is prepared by melting in a crucible a mixture of equivalent quantities of boric anhydride and acid chromate of potassium, whereby chromic borate and borate of potassium are obtained, and treating the fused mass with water, which resolves the chromic borate into boric acid and chromic hydrate. By washing this hydrate and finely triturating it, a brilliant green powder is obtained. (**Guignet**, Rép. Chim. app. 1859, p. 158.)

Arnandon (*ibid.* 201), by acting on acid chromate of potassium with phosphate of ammonium, likewise obtained a very fine green pigment, which appeared to be chiefly a chromic hydrate containing phosphoric acid.

For further details respecting the modifications of chromic hydrate, see Handw. d. Chem. 2^te^ Aufl. ii. [2] 1221.

Chromic Salts.—The salts obtained by dissolving chromic oxide or hydrate in acids, correspond in composition to the oxide itself, containing, that is to say, 3 at. of monatomic acid radicle to 2 at. of chromium, or 3 at. of a diatomic acid radicle to 4 at. chromium, *e.g.* the nitrate $Cr^2(NO^3)^3$, the sulphate $Cr^4(SO^4)^3$. The most definite are the double sulphates, called chrome-alums, consisting of 1 at. chromic sulphate with 1 at. sulphate of an alkali-metal and 12 at. water, corresponding in composition to common alum, and crystallising in the same form, *e.g.* potassio-chromic sulphate,

$$K^2SO^4.Cr^4(SO^4)^3 + 12H^2O, \text{ or } KCr^2(SO^4)^2 + 6H^2O = \left.\begin{matrix}(S^2O^4)^{iv}\\ K(Cr^2)^{'''}\end{matrix}\right\}O^4 + 6H^2O.$$

Chromic salts exhibit two modifications, the **green**, and the **red**, or **violet**, which pass easily one into the other. Thus, a solution of chrome-alum prepared in the cold has a violet colour, which changes to green on heating the solution, but reappears after it has been left to itself for some time. In many chromic salts the nitrate, for example, the change from green to violet takes place very quickly. The green solutions also take a bluish tint when heated with nitric acid. The violet appears to be the normal modification, inasmuch as the others always pass into it after a while; and it is only the violet solutions that yield crystallisable salts, the green solutions, when evaporated, leaving green amorphous masses.

Schrötter (Pogg. Ann. liii. 13) supposes that the change from the violet to the green modification by heat, is the result of a loss of chemically combined water, which is gradually resumed when the green solution is left at rest. **Otto** (Lehrbuch, 3 Aufl. ii. 93) remarks, in opposition to this view, that a red solution of chrome-alum does not turn green when mixed with strong sulphuric acid, provided rise of temperature be prevented.

Löwel (J. pr. Chem. xxxvii. 38) supposes that the different coloured solutions contain different proportions of acid and base, the red solutions containing normal chromic salts, such as $Cr^4(SO^4)^3$, or $Cr^4O^3.3SO^3$, and the green solutions basic salts of the form $Cr^4O^3.2SO^3$. This view receives some support from an observation of **Krüger** (Pogg. Ann. lxi. 218), that when a green solution of chrome-alum, obtained by boiling the salt with a very small quantity of water, is mixed with alcohol, the alcohol takes up a portion of the sulphuric acid, while the separated syrupy liquid contains the salt $K^2O.Cr^4O^3.3SO^3$. This salt, when dissolved in water, does not return to the violet modification unless a quantity of sulphuric acid be added to it sufficient to reproduce the normal salt $K^2O.Cr^4O^3.4SO^3$.

Frémy attributes the change of the violet salts into green by the boiling of their solutions, to a conversion of metachromic oxide into ordinary chromic oxide; this, however, can scarcely be called an explanation.

For the behaviour of chromic salts with reagents see pp. 943, 944.

Chromites.—Chromic oxide unites with protoxides, forming compounds of the form $M^2O.Cr^4O^3$, or MCr^2O^2, which may be called chromites. The best known of these compounds is chrome-iron ore, in which, however, part of the chromium is usually replaced by aluminium and sometimes by iron. Lime, magnesia, and oxide of zinc, when they exist in solution with chromium, are sometimes precipitated by alkalis, when, if the chromium were not present, they would remain dissolved; thus, a solution of chrome-alum mixed with chloride of calcium yields with ammonia a green precipitate, consisting of $2Ca^2O.Cr^4O^3$. On the other hand, bases which would otherwise be precipitated are sometimes retained in solution through the medium of chromic oxide; this is often the case with manganous and ferric oxide. In presence of 80 per cent. ferric oxide, however, chromic oxide is completely precipitated. These circumstances require to be carefully borne in mind in analysis.

Compounds of Chromic Oxide with Ammonia. (**Frémy**, Ann. Ch. Pharm. cx. 226.)—Chromic hydrate is slightly soluble in ammonia, and, under certain circumstances, takes up the elements of ammonia, forming peculiar metallic bases, designated by Frémy as **amido-chromium compounds.**

Chromic hydrate which has been subjected to the action of boiling water does not act upon ammonia; but metachromic hydrate (p. 950), in contact with ammonia, acquires a violet colour, and forms the compound containing $2NH^3.Cr^4O^3$, which gives off the whole of its ammonia when heated.

Ammoniacal salts do not act on metachromic hydrate by themselves; but if ammonia is likewise present, the hydrate dissolves, forming compounds of a beautiful violet colour, which may be obtained in definite form by precipitating with alcohol and rapid drying in vacuo. The compound formed with ammonia and chloride of ammonium dissolves in water with deep violet-red colour. The solution has a scarcely perceptible alkaline reaction, and does not yield any precipitate with nitrate of silver; but if it be heated to the boiling point, ammonia is given off, chromic hydrate separates out, and the remaining liquid then gives a copious precipitate with nitrate of silver. The products of the decomposition are $4NH^4Cl$, $8NH^3$, $3Cr^4O^3$, and H^2O.

If the solution of the amido-chromium compound be left to itself for a while, it decomposes, ammonia being evolved, sal-ammoniac being reproduced, and an insoluble violet body being formed, which separates in round, transparent, iridescent granules. This body likewise contains the elements of chromic oxide and ammonia. It is completely decomposed by boiling water, the products of decomposition being in the ratio of $Cr^4O^3 : 2NH^3 : 12H^2O$. Acids convert it into a basic compound, $Cr^4O^3.8NH^3$, called **roseo-chromammonia**. With sulphuric acid the reaction is:

$$4(Cr^4O^3.2NH^3) + 12H^2SO^4 = \underbrace{(Cr^4O^3.8NH^3).3SO^3}_{\substack{\text{Sulphate of roseo-}\\ \text{chromammonia.}}} + \underbrace{3(Cr^4O^3.3SO^3)}_{\substack{\text{Chromic}\\ \text{sulphate.}}} + 12H^2O.$$

Roseo-chromammonia may likewise be obtained by the action of strong acids in the cold on the soluble amido-chromium compounds precipitated by alcohol from the rose-coloured liquids which are produced by the joint action of ammonia and ammonium-salts on metachromic hydrate. The salts of this base have nearly a wine-red colour; the hydrochlorate crystallises in regular octahedrons, and forms crystallisable double salts with mercuric and platinic chlorides. Pure water decomposes it into two new salts, one crystallising in right rhombic prisms, the other remaining in solution. The bases of these two salts appear to differ from each other, and likewise from that of the hydrochlorate from which they were produced. (Frémy.)

A basic compound containing $Cr^2(CNS)^3.(NH^4)^2O$ is obtained, by adding acid chromate of potassium to fused sulphocyanate of ammonium. (Morland, Chem. Soc. Qu. J. xiii. 252.) (See SULPHOCYANATES.)

BROWN OXIDES OF CHROMIUM. CHROMATES OF CHROMIUM.—These names are applied to certain oxides intermediate between the sesqui- and tri-oxides of chromium. They are obtained by gently heating chromic nitrate; by partial reduction of chromic anhydride with alcohol, sulphurous acid, nitric oxide, or ferrous sulphate; also by boiling a solution of chromate of ammonium; by digesting chromic acid with excess of chromic oxide; by heating chromic anhydride above 250° C.; and by keeping chromic oxide for some time, at 200° C., in contact with the air. A solution of acid chromate of potassium, mixed with ammonia or with alcohol, likewise deposits a brown sediment when exposed to sunlight, but not in the dark.

These brown compounds, when heated, first give off water, if they are hydrated, and at higher temperatures are reduced to chromic oxide; they dissolve in acids, forming brown solutions, from which they are precipitated by ammonia without alteration. They give off chlorine when heated with hydrochloric acid. Alkalis separate chromic acid from them.

The brown oxides, obtained by different processes, exhibit considerable diversity of composition, and it is not exactly known whether they are distinct oxides of chromium or compounds of the sesqui- and tri-oxides. The compound obtained by heating chromic hydrate in contact with the air, which has the composition CrO, or $Cr^4O^3.Cr^2O^3$, is regarded by Krüger as a peroxide of chromium, CrO, because, when heated with sulphuric acid and chloride of sodium, it gives off only chlorine and no chlorochromic anhydride, as all chromates do. A precipitate of the same composition is formed, according to Berzelius, on mixing neutral solutions of chromic chloride and chromate of potassium. The precipitate thrown down by ammonia from a solution of chromic sulphate mixed with acid chromate of potassium, likewise gives off nothing but chlorine when similarly treated; according to Vogel, it is $2CrO.H^2O$. The black substance obtained by heating chromic anhydride to 200° C. is, according to Traube, normal chromate of chromium, $Cr^4O^3.3Cr^2O^3$. It becomes soluble by boiling in water, imparting to the water, first a yellowish, then a deep brown colour.

The precipitate formed on mixing the solutions of chrome-alum and neutral chromate of potassium has, when dried at 100° C., the composition $3Cr^4O^3.2Cr^2O^3.9H^2O$. The oxide obtained by reducing chromic anhydride with alcohol, has, according to Traube, the same composition. It is insoluble in water; dissolves in hydrochloric acid with yellow, in nitric and in hot dilute sulphuric acid with brown colour. The solutions yield with ammonia a precipitate of sesquioxide, while chromic acid remains in solution. Potash quickly resolves it into chromic oxide and chromic acid.

Chromic hydrate digested with excess of chromic acid, yields a dark brown solution, which dries up to a residue soluble in alcohol, and containing, according to Maus, $Cr^4O^3.4Cr^2O^3$, or Cr^4O^5. (Handw. d. Chem. 2^{te} Aufl. ii. [2] 1236.)*

TRIOXIDE OF CHROMIUM. CHROMIC ANHYDRIDE. *Anhydrous Chromic Acid.* Cr^2O^3.—This oxide may be regarded as a constituent of the chromates, the formula of a neutral chromate being $MCrO^2$, or $M^2O.Cr^2O^3$. It is obtained in the free state:

a. By decomposing trifluoride of chromium with a small quantity of water.—The vapour of the trifluoride, evolved by distilling chromate of lead and fluor spar with fuming sulphuric acid, is passed into a large platinum crucible, slightly moistened on the inside and closed with moist paper. The trifluoride is then decomposed by the aqueous vapour, with which the air in the crucible is charged, into hydrofluoric acid and beautiful red needles of chromic anhydride, which fill the crucible.

b. By decomposing a chromate with sulphuric acid.—Chromic acid is easily prepared by pouring 1 vol. of a saturated solution of acid chromate of potassium in a thin stream into 1½ vol. strong sulphuric acid, stirring all the while. As the liquid cools, chromic anhydride crystallises from it in splendid crimson needles often an inch long. The mother-liquor is decanted, and the crystals are drained on a porous tile till they are nearly dry, and then purified by recrystallisation. For many purposes for which chromic acid is used, the presence of a certain quantity of sulphuric acid is not objectionable, so that the purification may be dispensed with.

Bolley (Ann. Ch. Pharm. lvi. 113) prepares chromic anhydride by dissolving a weighed quantity of acid chromate of potassium in a small quantity of boiling water, and adding to the hot solution the exact quantity of sulphuric acid required to form acid sulphate of potassium. The mixture when left to cool, solidifies for the most part into a red granular mass consisting of acid sulphate of potassium with adhering chromic anhydride. The mixture is stirred to cause the granular mass to subside; the solution is decanted; and the residual acid sulphate is washed several times with cold water. There then remains an orange-coloured sulphate of potassium with very little chromic acid, the greater part of that acid being contained in the united solutions. The separation thus effected depends upon the circumstance that acid sulphate of potassium, which dissolves very freely in boiling water (2 pts. of the salt to 1 pt. of water), is but sparingly soluble at ordinary temperatures, and cold water removes sulphuric acid from it with scarcely any potash, leaving neutral sulphate of potassium, while the chromic acid dissolves in the cold water. The solution of chromic acid containing only a small quantity of acid sulphate of potassium is then further concentrated, and the chromic anhydride is precipitated by adding about an equal volume of strong sulphuric acid, which throws it down free from any trace of acid sulphate.

Chromic anhydride may also be prepared by decomposing chromate of lead with strong sulphuric acid, diluting with water after twenty-four hours, to precipitate sulphate of lead, then filtering and evaporating to the crystallising point, or by decomposing chromate of barium with strong nitric acid, filtering the liquid from the resulting nitrate of barium, which is insoluble in the strong acid, and heating the filtrate till the excess of nitric acid is expelled, and crystallising as above.

Pure chromic anhydride forms either a red powder, a red loose woolly mass, or scarlet crystals. It deliquesces in damp air and dissolves in a small quantity of water, forming a dark brown liquid having a sour astringent taste and yellow or brownish yellow on dilution. The solution contains chromic acid, but when evaporated it yields the anhydride: indeed chromic acid is not known in the solid state.

Chromic anhydride melts at 190° C., and begins to decompose at 250°, giving off oxygen and leaving a brown oxide or chromate of chromium, which, when further heated, is reduced to sesquioxide. Chromic anhydride is a powerful oxidising agent, being quickly reduced to sesquioxide of chromium by *sulphydric acid*, *zinc*, *arsenious acid*, *tartaric acid*, *sugar*, *alcohol*, and various other organic bodies, especially when heated. With *sulphydric acid* it forms water and sets sulphur free: $2Cr^2O^3 + 3H^2S = Cr^4O^3 + 3H^2O + S^3$; with *hydrochloric acid* it yields sesquichloride of chromium, water, and free chlorine: $Cr^2O^3 + 6HCl = Cr^2Cl^3 + 3H^2O + Cl^3$. *Sulphurous acid* added to a solution of chromic acid or a chromate throws down a brown chromate of chromium, consisting of $Cr^4O^3.Cr^2O^3$ or CrO. A few drops of *anhydrous alcohol* poured upon chromic anhydride instantly reduce it to sesquioxide, the alcohol sometimes taking fire. A similar reduction attended with incandescence

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* From recent experiments by Storer and Eliot (Proc. Amer. Acad. v. 192), it appears that there is but one definite oxide of chromium intermediate between Cr^4O^3 and Cr^2O^3, viz. CrO or $Cr^4O^3.Cr^2O^3$. The authors have likewise obtained the analogous compounds $Al^4O^3.Cr^2O^3$, $Fe^4O^3.Cr^2O^3$, $Mn^4O^3.Cr^2O^3$.

takes place when a small quantity of the anhydride is introduced into an atmosphere of alcohol vapour, or of alcohol or ether vapour mixed with sulphide of carbon. Dry *ammonia gas* suddenly directed upon perfectly dry chromic anhydride, renders it incandescent and converts it into chromic oxide, while nitrogen and aqueous vapour are given off. Aqueous chromic acid bleaches vegetable colours.

Chromic acid in the free state is sometimes used practically as an oxidisng agent, but more frequently a mixture of sulphuric acid and chromate of potassium, which yields it.

When crystallised chromic anhydride is added to strong sulphuric acid as long as it dissolves, an ochre-yellow, pasty, very hygroscopic substance is formed, containing. according to Bolley (Ann. Ch. Pharm. lvi. 113), $H^2SO^4.Cr^2O^3$. When exposed to the air, it quickly turns red from separation of chromic anhydride. Schrötter (Pogg. Ann. lix. 616) obtained in like manner a yellow-brown sediment, which he represents approximately by the formula $Cr^4O^3.3SO^3$.

Perchromic Acid. HCr^2O^4 or $H^2O.Cr^4O^7$?—When peroxide of hydrogen dissolved in water is mixed with a solution of chromic acid, the liquid assumes a deep indigo-blue colour, but often loses this colour very rapidly, giving off oxygen at the same time. The same blue colour is produced on adding a mixture of aqueous peroxide of hydrogen and sulphuric or hydrochloric acid to acid chromate of potassium; but in a very short time oxygen is evolved, and chrome-alum is left in solution. For each atom of acid chromate of potassium, $K^2O.2Cr^2O^3$, 4 at. of oxygen are evolved, provided an excess of peroxide of hydrogen be present. We may, therefore, suppose that perchromic acid, HCr^2O^4, is first formed by the union of HO with Cr^2O^3, and afterwards resolved into oxygen and chromic hydrate, $2HCr^2O^4 = H^2O.Cr^4O^3 + O^4$. With ether, perchromic anhydride forms a more stable solution than with water. The ethereal solution, which has a deep blue colour, may be obtained by treating peroxide of barium with hydrochloric or nitric acid, pouring ether on the liquid, gradually adding a solution of acid chromate of potassium, and agitating. Perchromic acid is decomposed by aqueous alkalis, with formation of a chromate and evolution of oxygen; but ammonia and certain organic bases dissolved in ether and added to the ethereal solution of the acid, form stable compounds, from which stronger acids separate the blue acid. The most stable of these compounds is the quinine-salt, which is soluble in alcohol, insoluble in ether, and may be dried without decomposition. (Barreswil, Compt. rend. xvi. 1085.)

The recent investigations of Aschof (*Inaugural-Dissertation über die Uebermangansäure und Ueberchromsäure*, Berlin, 1861) tend strongly to confirm the formula Cr^4O^7 for hypothetical perchromic anhydride. He also finds that when the deep blue ethereal solution of perchromic acid is shaken up with such a quantity of very dilute aqueous potash, that the ethereal layer shall still exhibit a faint blue tint, the aqueous, perfectly neutral liquid below exhibits a peculiar deep bluish-violet tint, which is tolerably stable; but if more potash be added, the colour changes to the light yellow of neutral chromate of potassium, while bubbles of oxygen are given off. Hence it appears that the blue colour belongs to the free acid, the violet to its salts.

According to Storer (J. pr. Chem. lxxxi. 44) the colouring power of perchromic acid is so great, that when a solution of 1 pt. acid chromate of potassium in 30,000 to 40,000 pts. water is shaken up with ether containing peroxide of hydrogen, the ether acquires a perceptible blue tint; he therefore recommends this reaction as a very delicate test for chromic acid. Schönbein (*ibid.* lxxix. 65) applies it as a test for peroxide of hydrogen.

CHROMIUM, OXYCHLORIDES OF. Four of these compounds are known, three of which may be regarded as compounds of sesquioxide and sesquichloride of chromium, and the fourth (the so-called *chlorochromic acid*), as a compound of the trichloride and trioxide. They may also be regarded as derived from the trichloride or sesquichloride by the substitution of oxygen for part of the chlorine.

a. Compounds of Sesquichloride and Sesquioxide of Chromium.—These compounds, of which three have been distinguished, are obtained by evaporating the green solution of the sesquichloride, and heating the residue to different temperatures. By drying at 120° C. a reddish tumefied mass is left, containing $8Cr^2Cl^3.Cr^4O^3 + 24H^2O$, or $Cr^{20}Cl^{24}O^3 + 24H^2O$.

By drying at 150° C., with constant stirring, a greyish red deliquescent powder is obtained, consisting of $4Cr^2Cl^3.Cr^4O^3 + 8H^2O = 3Cr^4Cl^4O + 8H^2O$, or, according to Péligot, $2(CrOCl.HCl) + H^2O$. If this compound be heated to redness, it becomes partially insoluble in water, and the undissolved portion consists of $Cr^2Cl^3.Cr^4O^3$, or Cr^2OCl. It is greyish-red by daylight, green by lamplight, like neutral chromic sulphate. By prolonged ignition in contact with the air, it is completely converted into sesquioxide. (Moberg.)

Péligot (J. pr. Chem. xxxvii. 476) obtained the last mentioned oxychloride by precipitating a green solution of chromic chloride with baryta, evaporating the filtrate to dryness, treating the residue with alcohol, and evaporating in vacuo, as a green deliquescent mass containing $2Cr^2OCl + 3H^2O$. The same oxychloride is obtained by boiling the green solution of the chloride with chromic hydrate, or by prolonged boiling of dilute hydrochloric acid with excess of chromic hydrate.

b. Chlorochromic Anhydride, Chlorochromic Acid. $CrOCl$, or $CrCl^3.Cr^2O^3$.—This compound, discovered by Berzelius, is produced by distilling any anhydrous metallic chloride with an anhydrous chromate and strong sulphuric acid; its formation affords a useful test for the presence of chlorides (p. 903). To prepare it, 10 pts. of decrepitated chloride of sodium are fused with 16·9 pts. of neutral chromate of potassium, and the fused mass, after being broken into lumps, is distilled in a tubulated retort with 30 pts. of strong sulphuric acid, or better with the fuming acid. A brisk action immediately takes place, and the chlorochromic anhydride quickly distils over, without application of heat; it must be collected in a dry receiver kept at a low temperature. The distillate obtained by heating the mixture towards the end of the process, is likely to be contaminated with chromic and sulphuric acids (Wöhler, Pogg. Ann. xxxiii. 343). Another and easy mode of preparation is to distil in a small retort a dry mixture of chromic anhydride and ferric chloride. (Geuther, Ann. Ch. Pharm. cvi. 239.)

Chlorochromic anhydride is a mobile liquid of a splendid blood-red colour by transmitted light, nearly black by reflected light. It has a density of 1·71, and boils at 118° C. When exposed to the air, it diffuses a yellowish-red vapour of specific gravity 5·48. It attacks *mercury* rapidly, detonates with *phosphorus*, sets fire to *sulphur*, *alcohol*, *oil of turpentine*, and other inflammable bodies, and decomposes *sulphydric acid*, with emission of light. In *ammonia gas*, it solidifies with brilliant incandescence, forming a dark brown mass, which remains red-hot for some time. If more ammonia gas be passed over the ignited residue, it changes to a black powder, which, according to Schrötter, is nitride of chromium. When chlorochromic anhydride is distilled with *pentachloride of phosphorus*, chlorine-gas is evolved, and a small quantity of sesquichloride of chromium is formed, but the greater part of the chlorochromic anhydride distils without alteration. It dissolves *iodine* and forms a solid brown mass with *chlorine*. When dropped into *water*, it remains unaltered for a few seconds, but is afterwards decomposed, with violent ebullition, into chromic and hydrochloric acids.

Vapour of chlorochromic anhydride passed through a glass tube heated to low redness is decomposed, with formation of crystalline chromic oxide (p. 948).

The compound described at page 938 as chromochloride of potassium, may be regarded as a compound of chlorochromic anhydride with neutral chromate of potassium, $KCrO^2.CrOCl$.

CHROMIUM, OXYGEN-SALTS OF. See Chromous and Chromic Oxides (pp. 947, 950); also the several Acids.

CHROMIUM, PHOSPHIDE OF. Cr^2P.—Formed when chromic phosphate is strongly ignited with charcoal, or when sesquichloride of chromium is heated in phosphoretted hydrogen gas. The product obtained by the first process is light grey, with faint lustre, and loosely coherent. The phosphide prepared from crystallised chromic chloride forms crystalline scales, like those of the chloride itself; it is black, dissolves but slightly in nitric, nitromuriatic or hydrofluoric acid, oxidises slowly when heated in the air; when it is heated with hydrate of potassium, hydrogen is evolved, and chromate of potassium very slowly formed. (H. Rose, Pogg. Ann. xxxiv. 333.)

CHROMIUM, SULPHIDES OF. The *protosulphide*, Cr^2S, is said to be obtained, mixed with chromic oxide, by heating chromic sulphate in dry oxygen gas (Traube). According to Moberg, protochloride of chromium gives a black precipitate with sulphide of ammonium.

The *sesquisulphide*, Cr^4S^3, is produced by passing vapour of sulphide of carbon over the white-hot sesquioxide; by passing dry sulphydric acid gas over chromic anhydride, oxide, or chloride, heated to bright redness; by heating chromic hydrate with sulphur in vacuo; or by melting chromic oxide with pentasulphide of potassium at a very high temperature. It cannot be obtained by precipitation, the precipitate formed by sulphide of ammonium in solutions of chromic salts, consisting, not of sulphide, but of hydrate.

Sesquisulphide of chromium is dark grey or black, according to the mode of preparation, sometimes shining and crystalline, without metallic appearance, but acquiring an iron-grey metallic lustre by pressure or trituration. When heated in the *air*, it burns to sesquioxide. Heated in *chlorine gas*, it yields chloride of sulphur and sesquichloride of chromium (Berzelius). According to H. Rose, on the other hand, chlorine scarcely acts upon it, even at high temperatures. Heated with *nitre*, it yields sulphate and chromate of potassium. It appears to unite with the acid sulphides, forming sulphur-salts. (Gm. iv. 124.)

A sulphide containing Cr^2S^3 is obtained by heating chromic sulphate in hydrogen gas. Sulphurous anhydride is then evolved and sulphuric acid is formed, together with a blackish-brown, extremely pyrophoric powder, which burns in the air to chromic oxide and sulphurous anhydride. (Kopp, Compt. rend. xix. 1156.)

CHROMOTARTARIC ACID. When tartaric acid in powder is gradually added to a warm aqueous solution of acid chromate of potassium, as long as carbonic acid is evolved, a green solution is formed, which yields by evaporation a vitreous mass, very soluble in water, precipitated by alcohol, and containing, according to Malaguti, $C^4H^4K(Cr^2O)'O^6 + 7aq$. The solution of this salt yields with acetate of lead, a bluish-green precipitate, which, when decomposed by sulphuretted hydrogen, yields tartrate of chromium and hydrogen, or *chromo-tartaric acid*, $C^4H^5(Cr^2O)'O^6$. (Berlin, *Gerhardt's Traité*, ii. 31.)

CHROMULE. Syn. with CHLOROPHYLL.

CHRYIODINE. A product of the decomposition of chrysammic acid by sulphuric acid. (See CHRYSAMMIC ACID.)

CHRYSAMIDE. $C^7H^3(NO^2)^2NO = N.H^2.C^7H(NO^2)^2O$. — A compound formed by boiling chrysammic acid with aqueous ammonia. The acid dissolves; the liquid acquires a deep purple tint, and on cooling deposits chrysamide in needles, which are reddish-brown by transmitted, and metallic green by reflected light. Its solution, treated with dilute acids, does not yield a precipitate of chrysammic acid. With chloride of barium and ammonia, it forms a precipitate of chrysamidate of barium.

According to the formula $C^7H^3(NO^2)^2NO$, which is that proposed by Gerhardt (*Traité*, iv. 253), chrysamide, like amides in general, differs from chrysammate of ammonium, $C^7H(NH^4)(NO^2)O^2$, by 1 at. H^2O. This formula requires 40 per cent. C, 2·4 H, and 20·1 N, whereas the analysis of chrysamide by Schunck and Mulder, gives 37·6 – 38·8 C, 1·85 – 2·35 H, and 18·2 – 19·9 N; but it is probable that the chrysamide analysed was partly converted during the preparation into chrysamidic acid by addition of water, or rather perhaps, that the conversion of the chrysammate of ammonium into chrysamide was not quite complete.

CHRYSAMIDIC ACID. *Ammonio-chrysammic acid.* $C^7H^5N^3O^6 = NH^3.C^7H^2(NO^2)^2O^2$.—This acid, which is isomeric with chrysammate of ammonium, is produced by adding dilute sulphuric or hydrochloric acid to a boiling aqueous solution of chrysamide, and crystallises on cooling in dark-coloured needles, which become olive-green on drying. Its aqueous solution has a deep purple colour, from which it is partly precipitated by acids without change of colour. It gives off ammonia when treated with potash. It is not altered by dilute acids. Strong sulphuric and boiling nitric acid partly convert it into chrysammic acid, with formation of ammoniacal salts.

The chrysamidates, $C^7H^4MN^3O^6$, have the composition of double chrysammates of ammonium and another base, $C^7(NH^4)MN^2O^6$ They resemble the chrysammates in appearance, and in their property of detonating when heated; but are distinguished by giving off ammonia when treated with caustic potash.

Chrysamidate of potassium crystallises in small needles, having a green metallic lustre by reflected light. The *barium-salt* is a red crystalline precipitate.

CHRYSAMMIC ACID. $C^7H^2N^2O^6 = C^7H^2(NO^2)^2O^2$. (Schunck. Ann. Ch. Pharm. xxxix. 1; lxv. 235. — Mulder, *ibid.* lxxiii. 339; lxxii. 285. — Laurent, Compt. chim. 1850, p. 163.—Robiquet, J. Pharm. [3] x. 167, 241). — This acid is produced by the action of nitric acid upon aloes; probably, also by the action of nitric acid on aporetin. (De la Rue and Müller, Chem. Soc. Qu. J. x. 298.)

Preparation from aloes.—1 pt. of aloes is macerated with 8 pts. of nitric acid of specific gravity 1·37; the mass is heated in a large basin till the first violent action has subsided, afterwards in a retort till two-thirds of the nitric acid have been expelled; 3 or 4 pts. more nitric acid and water are added to the residual liquid as long as a precipitate continues to form; and the precipitate, which consists of small shining scales, is washed with cold water till the liquid no longer acquires a yellow, but a faint purple-red colour. The resulting chrysammic acid, still containing aloëtic acid, is triturated with aqueous carbonate of potassium; and the gelatinous mass, which is thereby formed, with evolution of carbonic acid, is washed with cold water till the whole of the carbonate of potassium is removed, then dissolved in boiling water, and the solution filtered; as the liquid cools, the pure potassium-salt separates in golden-yellow laminæ. These crystals are dissolved in boiling water, decomposed by nitric acid, and the chrysammic acid, which separates in the form of a yellow powder, is washed with cold water till the nitric acid is completely removed, and the water is coloured no longer yellow but light purple-red. In treating the chrysammic acid with carbonate of potassium, an excess of the latter must be avoided as far as possible, because it produces a decomposition and reddening of the salt, perhaps from admixture of aloëtic acid.

Chrysammic acid is a yellow powder, often light yellow or greenish yellow, and consisting of small shining scales. It is sparingly soluble in cold, more easily in boiling water. The solution has a deep purple colour, tastes bitter, and reddens litmus. It dissolves easily in alcohol and ether; also in nitric acid and in saline solutions.

The acid detonates violently when subjected to dry distillation, emitting a bright but smoky flame, and diffusing an odour of bitter almonds, together with nitrous vapours. Heated in *chlorine gas*, it gives off hydrochloric acid. Boiled with *caustic potash*, it forms a brown solution from which acids throw down a dark brown precipitate (Schunck's *aloeretic acid;* Mulder's *chrysatic acid*), soluble in pure water, forming soluble salts with the alkalis and earths, insoluble with lead and silver. If the potash is very strong, ammonia is likewise evolved. Chrysammic acid is not attacked by *fuming nitric acid* (Schunck). With strong *sulphuric acid* at the boiling heat, it reacts violently, giving off copious red fumes containing carbonic anhydride, carbonic oxide, sulphurous anhydride, and nitrous anhydride. At the same time a dark violet-coloured substance is deposited (Mulder's *chryiodine*), soluble in potash and reprecipitated by hydrochloric acid, as a gelatinous mass of the same colour. This product appears to be only a mixture, for ammonia separates it into a soluble and an insoluble portion. *Sulphide of potassium* mixed with caustic potash, transforms chrysammic acid into hydrochrysamide: a similar blue substance (Mulder's *chrysindinammonium*) is obtained by decomposing a warm ammoniacal solution of chrysammic acid with sulphuretted hydrogen. *Ammonia* converts chrysammic acid into chrysamide. The acid boiled with water and *stannous chloride*, forms a powder which has a deep violet colour, is nearly insoluble in all solvents ($C^{11}H^{4}N^{2}O^{11}.3SnO^{2}$, according to Mulder), gives off ammonia and assumes a fine blue colour when treated with potash, and is decomposed by nitric acid, yielding aloëtic and chrysammic acids.

The **chrysammates** mostly crystallise in small scales, and exhibit a gold-green metallic lustre on the crystalline faces; those which are amorphous, exhibit the same lustre when rubbed with a hard body. They detonate violently when heated. They are all sparingly soluble, even those of the alkali-metals. In solutions of acetates they dissolve more easily than in water, but less when heated than in the cold.

Chrysammate of Ammonium changes rapidly into chrysamide.

Chrysammate of Barium, $C^7HBaN^2O^6 + 2aq.$, is obtained as a vermilion-coloured precipitate by mixing a solution of the potassium-salt with chloride of barium; also by prolonged boiling of chrysammic acid with chloride of barium. It is quite insoluble in water.

Chrysammate of Cadmium is a dark purple precipitate.

Chrysammate of Calcium is a dark red insoluble powder, exhibiting traces of crystallisation.

Chrysammate of Copper, $C^7HCuN^2O^6 + x\,aq.$, is sparingly soluble in cold, more soluble in boiling water, from which it separates in dark purple needles, exhibiting a golden lustre by reflected light: its solution has a fine purple tint.

Chrysammate of Lead, $C^7HPbN^2O^6$? — Brick-red insoluble powder, obtained by precipitation. According to Schunck, it gives by analysis 34·2 per cent. Pb^2O, the formula requiring 35·78. Mulder found in the precipitate formed with chrysammate of potassium and neutral acetate of lead, 51·6 per cent. Pb^2O, which corresponds to the formula $C^7HPbN^2O^6.PbHO$.

Chrysammate of Magnesium resembles the calcium-salt.

Chrysammate of Potassium, $C^7HKN^2O^6$, crystallises in flat rhomboïdal plates, which exhibit very remarkable relations to polarised light. Light transmitted through one of them, exhibits a reddish-yellow colour and becomes polarised in one plane; but if the crystal be pressed with the blade of a knife on a plate of glass, it spreads on the glass like an amalgam, and a beam of light, transmitted through the thin film thus formed, splits into two rays polarised in planes perpendicular to each other, one having a carmine-red, the other a pale yellow colour. As the thickness of the film increases, the colour of both rays approaches more and more to carmine-red. Still more remarkable phenomena are exhibited by reflected light. An ordinary ray of white light reflected perpendicularly from the face of a crystal or from a film, has the colour of virgin-gold, but as the incidence becomes more oblique, the colour becomes less and less yellow, and at length passes into pale blue. The beam thus reflected is composed of two rays oppositely polarised; the one which is polarised in the plane of reflection remains of a pale blue colour at all angles of incidence; the other, polarised at right angles to the plane of reflection, has a pale-yellow colour at small inclinations, then changes to deep yellow, greenish-yellow, green, bluish-green, blue and violet. (Brewster, *Gerhardt's Traité*, iv. 251.)

Chrysammate of potassium dissolves in 1250 pts. of cold water, easily in boiling water; the solution has a fine red colour.

Chrysammate of Silver. Dark brown precipitate, quite insoluble in boiling water.

Chrysammate of Sodium resembles the potassium-salt in appearance, and possesses the same degree of solubility.

Chrysammate of Zinc crystallises in small dark red needles with gold-green reflection.

CHRYSANILIC ACID. This name was given by Fritzsche to a bluish-red substance obtained by the action of potash upon indigo; according to Gerhardt however (*Traité*, iii. 521), it is nothing but a mixture of isatin, white indigo, and possibly other products. (See INDIGO.)

CHRYSANISIC ACID. $C^7H^5N^3O^7 = C^7H^5(NO^2)^3O$ (Cahours, Ann. Ch. Phys. [3] xxvii. 454).—This acid, which is isomeric with trinitranisol, and may also be regarded as methyl-picric acid, $C^6H^2(CH^3)(NO^2)^3O$, is produced, together with di- and tri-nitranisol, by the action of warm fuming nitric acid on anisic acid (p. 300). When 1 pt. of perfectly dry anisic acid is very gently boiled for half or three-quarters of an hour with 2½ pts. of fuming nitric acid, and the somewhat thick liquid is mixed with 20 times its bulk of water, a yellow oil separates out, which soon coagulates into a solid mass consisting of chrysanisic acid mixed with di- and tri-nitranisol. This mixture, in the form of fine powder, is washed on a filter with ammonia diluted with two or three times its bulk of water, whereby the acid is extracted; the ammoniacal liquid, after being evaporated to one-third, yields on cooling brown needles of the ammonia-salt. These crystals are dissolved in water; the solution mixed with dilute hydrochloric acid; the separated yellow flakes are collected on a filter, repeatedly washed with cold water, dried between bibulous paper, and dissolved in hot alcohol; and the scales which crystallise from the solution on cooling are dried.

Chrysanisic acid forms small golden-yellow rhombic tables, nearly insoluble in cold water, sparingly soluble in hot water, whence it crystallises on cooling. It is but slightly soluble in cold alcohol, but dissolves so abundantly in hot alcohol, that the liquid solidifies on cooling. It dissolves in ether, especially if hot, and crystallises in shining laminæ as the ether evaporates. The acid melts when cautiously heated, and solidifies in the crystalline form on cooling; at a stronger heat, it emits a yellow vapour which condenses in small crystalline scales having a strong lustre.

When boiled with strong nitric acid, it is converted into picric acid. Distilled with aqueous chloride of lime, it yields chloropicrin. By boiling with potash, it is converted into a brown substance.

Chrysanisate of Ammonium.—The solution of the acid in dilute ammonia, evaporated over the water-bath, yields on cooling, small brown needles having a strong lustre. Finer crystals are obtained by spontaneous evaporation of the solution.

Chrysanisate of Potassium, $C^7H^4K(NO^2)^3O$, is obtained by exactly saturating the acid with potash. It is very soluble.

The ammonium-salt produces in solutions of *zinc*-salts, a pale yellow precipitate; with nitrate of *cobalt*, a greenish yellow gelatinous precipitate; with nitrate of *lead*, a copious deposit of chrome-yellow flakes; with *ferric* salts, a pale yellow; with *cupric* salts, a greenish yellow, gelatinous precipitate; and with *mercuric chloride*, yellowish-red flakes, which in dilute solutions appear after a time only.

Chrysanisate of Silver, $C^7H^4Ag(NO^2)^3O$.—The ammonium-salt forms with nitrate of silver, beautiful yellow flakes, which must be washed with water and dried in vacuo.

Chrysanisate of Ethyl, $C^7H^4(C^2H^5)(NO^2)^3O$, is obtained by saturating the alcoholic solution of the acid with dry hydrochloric acid gas, gently boiling for some time, and then adding water. The resulting precipitate is washed, first with ammoniacal, afterwards with pure water, then dissolved in boiling alcohol, and the solution is left to cool. It forms transparent crystalline laminæ of a splendid golden-yellow colour, melting at about 100° C. It is soluble in warm *ether*.

CHRYSANTHEMUM SEGETUM. The ash of this plant has been analysed by Bangert (J. pr. Chem. lxx. 85).—The fresh plant yielded 1·61 per cent., the plant dried at 100° C, 8·52 per cent. ash (63·3 per cent. of which was soluble in water). The ash contained in 100 pts.: 24·86 K^2O, 6·21 Na^2O, 14·08 Ca^2O, 6·96 Mg^2O, trace of manganese, 5·12 SO^3, 12·36 CO^2, 6·16 P^2O^5, 4·68 SiO^2, 16;10 NaCl, with 3·06 sand and charcoal.

CHRYSATRIC ACID. (Mulder, J. pr. Chem. xlviii. 16.) *Aloeretic acid.* (Schunck, Ann. Ch. Pharm. lv. 240.)—An acid produced by heating chrysammic acid with alkalis. Chrysammic acid heated with potash-ley dissolves, forming a brown solution, from which, according to Mulder, acetic acid does not precipitate anything; according to Schunck, however, a brown precipitate is obtained. The solution of the potassium-salt yields with acetate of lead, a brown precipitate containing, according to Tonningen's analysis, 58·71 per cent. Pb^2O, 19·08 C, 0·78 H, and 5·51 N. With chloride of barium, a precipitate is formed, containing 30·80 per cent. Ba^2O, 28·03 C, and 1·82 H. (Schunck). These analyses do not lead to any satisfactory formula.

CHRYSENE, nC^6H^4. (Laurent, Ann. Ch. Phys. [2] lxvi. 136.) — A crystalline hydrocarbon obtained, together with *pyrene*, by the dry distillation of fats, resins, and coal: it may be extracted from coal-tar by redistillation. The products which pass over towards the end of the process, consist of a soft yellow or reddish mass, and a thick oil containing crystalline scales. That which condenses in the neck of the retort is chiefly chrysene, the pyrene passing for the most part into the receiver. By treating the mass in the neck of the retort with ether, the pyrene and certain oily matters are dissolved out, while the chrysene remains in the pulverulent state.

Pure chrysene has a fine yellow colour; it is crystalline, destitute of taste and odour, insoluble in water and alcohol, nearly insoluble in ether: oil of turpentine dissolves it at the boiling heat, and deposits it on cooling in yellow crystalline flakes. It melts at 230° — 235° C., and solidifies on cooling to a deep yellow mass composed of needles. At a higher temperature, it distils with slight alteration.

Nitrochrysene, $nC^6H^3(NO^2)$, produced by the action of strong boiling nitric acid on chrysene, is a red powder, destitute of taste and odour, insoluble in water, nearly insoluble in alcohol and ether. It is dissolved with brown colour by sulphuric acid, partially also by alcoholic potash. When quickly heated in a closed tube, it melts and decomposes with explosion.

CHRYSINDIN. A product of the decomposition of chrysammic acid by ammonia. (Mulder, p. 956.)

CHRYSOBERYL. *Cymophane, Chrysopal.*—An aluminate of glucinum, Al^2GlO^4, or $Gl^2O.Al^4O^6$, generally containing 2 or 3 per cent. of iron. It is usually found in round pieces about the size of a pea, but sometimes in eight-sided prisms with six-sided summits, belonging to the trimetric system. Specific gravity 3·5 — 3·7. Hardness 8·5. Lustre vitreous. Colour various shades of green. Streak uncoloured. Transparent or translucent, sometimes with bluish opalescence internally. Fracture conchoïdal, uneven. It exhibits double refraction, and becomes electric by friction. It is infusible alone before the blowpipe, and very difficult to fuse with borax or phosphorus-salt. With carbonate of sodium, the surface is merely rendered dull. It is not acted upon by acids.

Chrysoberyl is found in Brazil and Ceylon, in rolled pebbles, in the alluvial deposit of rivers; and in granite at Haddaw, Connecticut, Greenfield, near Saratoga, New York, and Orange Summit, Vermont. When transparent and of sufficient size, it is cut into facets and forms a gem.

Crystals of chrysoberyl have been formed artificially by exposing a mixture of alumina and glucina in the proper proportion, together with boracic acid as a flux, to the heat of a pottery furnace for several days, till the boracic acid is completely volatilised (Ebelmen, Ann. Ch. Phys. [3] xxii. 211; xxxiii. 34). [For the crystalline form of the artificial chrysoberyl, see Jahresber. d. Chem. 1851, p. 765.]

A variety of chrysoberyl called *Alexandrite*, from the Ural, exhibits pleochroism, viz. by perfectly white light, an orange-yellow colour in the direction of the longer diagonal of the base, colombo-red along the shorter diagonal, and emerald-green along the principal axis. (Haidinger, Pogg. Ann. lxxvii, 228.)

CHRYSOCOLLA. The Greek name for borax. Applied also to silicate of copper.

CHRYSOHARMINE. Syn. with NITROHARMALINE (*q. v.*)

CHRYSOIDIN. $C^7H^{22}O^4$?—A yellow colouring matter said to exist in very small quantity in asparagus-berries.

CHRYSOLEPIC ACID. Syn. with PICRIC ACID.

CHRYSOLITE. *Peridote, Olivin.* — A silicate of magnesium and iron, $(Mg;Fe)^4SiO^4$, occurring in basalt and lavas, in prismatic crystals of the trimetric system, also massive and compact or granular; colour olive and other shades of green. The term *Chrysolite* includes the transparent crystals of paler colour, while *Olivine* (so-called from the olive-green tint) is applied to imbedded masses or grains of inferior colour and clearness. (See OLIVINE.)

CHRYSOMELANE. Syn. with PLEONAST.

CHRYSOPAL. Syn. with CHRYSOBERYL.

CHRYSOPHANE. See CLINTONITE.

CHRYSOPHANIC ACID. *Chrysophane, Rhubarbaric acid, Rhubarbarin, Rhubarb-yellow, Rhein, Rheic acid, Rheumin, Rhaponticin, Rumicin,* $C^{10}H^8O^3$, or $C^7H^{10}O^2$. The yellow colouring principle of rhubarb and of the wall lichen (*Parmelia parietina*). It was first obtained in an impure state by Herberger, Dulk, and Brandes, afterwards analysed by Rochleder and Heldt (Ann. Ch. Pharm. xlviii. 12), who extracted the pure substance from the *Parmelia;* also by Döpping and Schlossberger (*ibid.* l. 215), by De La Rue and Müller (Chem. Soc. Qu. J. x. 298) and by Thann (Ann. Ch. Pharm. cvii. 324), who obtained it from rhubarb.

Preparation from Parmelia parietina.—The dried lichen is digested in the cold with alcoholic potash or ammonia; the dark red infusion is filtered and mixed with acetic acid; the bulky yellow flocks thereby precipitated are washed with water and redissolved in alcoholic potash, a certain quantity of resin then remaining undissolved; the liquid is again precipitated by hydrochloric acid; and the precipitate, after washing and drying, is redissolved in a small quantity of boiling absolute alcohol. The solution then deposits chrysophanic acid in the crystallised state.

From Rhubarb.—Dulk prepared chrysophanic acid from rhubarb by exhausting the root with alcoholic ammonia, precipitating with subacetate of lead, and decomposing the precipitate, suspended in alcohol, with sulphuretted hydrogen. Schlossberger and Döpping exhaust the pulverised rhubarb with 80 per cent alcohol; evaporate; redissolve in a small quantity of alcohol; add ether to the solution to precipitate certain resinous matters; evaporate the filtered solution to the crystallising point; and purify the chrysophanic acid thus obtained by repeated crystallisation from boiling absolute alcohol.

De la Rue and Müller find that chrysophanic acid may be extracted from rhubarb with much greater facility by means of benzene or the light hydrocarbons obtained from Burmese naphtha, these liquids dissolving it very readily, to the exclusion of the greater part of the other constituents. The crushed root is first macerated in water, which removes about 50 per cent. of soluble matter, then dried and treated with benzene in a Mohr's displacement apparatus; the greater part of the benzene is then distilled off; the residue, which becomes nearly solid on cooling, is pressed between blotting paper to remove the mother-liquor which contains erythroretin and a neutral fat; the crude chrysophanic acid thus obtained is redissolved in hot benzene, which leaves behind a reddish-yellow substance (*emodin*), an additional quantity of which separates as the solution cools; and the chrysophanic acid, which afterwards crystallises out, is further purified by recrystallisation from acetic acid, amylic alcohol, or common alcohol. The residuary rhubarb, thrown away in pharmaceutical laboratories after the preparation of the ordinary alcoholic tincture, may be advantageously used for the preparation of chrysophanic acid by this process, inasmuch as it contains about 2·6 per cent. of that acid, which is but slightly soluble in alcohol, especially in the weak spirit used in the preparation of the tincture. The dark coloured resinous sediment which separates from *Tinctura Rhei* when left to itself, is also rich in chrysophanic acid, and may be subjected to the same treatment.

Thann extracts the root of *Rumex obtusifolius* with ether; distils off the greater part of the liquid; washes the dark yellow-brown mass which separates on cooling with a small quantity of ether; dries it between bibulous paper; boils the residue with 90 per cent. alcohol; dissolves the dirty green granular mass which separates on cooling with alcohol, and precipitates by water, repeating the solution and precipitation several times; purifies the product by treatment with alcoholic ammonia and acetic acid, as in Rochleder and Heldt's process; then crystallises it from alcohol, and lastly from ether by slow evaporation.

Chrysophanic acid crystallises from benzene in six-sided tables (monoclinic), having a pale yellow or orange-yellow colour; from alcohol, amyl-alcohol, or glacial acetic acid, in moss-like aggregates of laminar crystals. It is sparingly soluble in cold water; dissolves in 224 pts. of boiling alcohol of 86 per cent.; in 1125 pts. of the same alcohol at 30° C. It is soluble also in ether and in oil of turpentine, coal-naphtha, benzene, and other hydrocarbons (*vid. sup.*) It melts without decomposition at 162° C. and solidifies in the crystalline form on cooling.

The formula of chrysophanic acid is not quite settled. The analyses by Rochleder and Heldt, and by Schlossberger and Döpping, approach nearly to the formula $C^{10}H^{8}O^{3}$, while those by De la Rue and Müller, and by Thann, agree better with $C^{7}H^{10}O^{2}$.

	Calculation. $C^{10}H^{8}O^{3}$	Rochleder and Heldt.	Schlossberger and Döpping.	De la Rue and Müller.	Thann.	*Calculation.* $C^{17}H^{10}O^{2}$
Carbon .	. 68·12	68·03	68·12	68·76	69·62	69·52
Hydrogen	. 4·54	4·57	4·59	4·25	4·39	4·12
Oxygen .	. 27·34	„	„	„	„	26·36
	100·00					100·00

Chrysophanic acid subjected to dry distillation, partly sublimes, while another portion becomes carbonised. Dilute nitric acid does not appear to act upon it, even at the boiling heat, but the strong acid converts it into a red substance. Strong sulphuric acid dissolves without decomposing it, and water precipitates it from the solution.

The acid dissolves in alkalis with fine deep purple colour: the reaction is very delicate, so that a dilute solution of chrysophanic acid may be used as a test for alkalis. Its solution in potash may be evaporated to dryness without alteration; but at a certain degree of concentration, it deposits blue or violet flocks, which redissolve in water or alcohol, forming red solutions. If the purple solution of the acid in moderately strong potash, together with the flocculent precipitate, be mixed with grape sugar and left to stand in a closed vessel, the alkali being in excess, the colour of the liquid gradually changes to brownish-yellow, and the precipitate disappears: on subsequent exposure to the air, the original colour and the precipitate are reproduced. Hydrate of potassium at its melting point does not act on chrysophanic acid at first; but if the heat be continued or increased, the liquid turns blue and decomposes, emitting an odour like that of octylic alcohol. (De la Rue and Muller.)

With baryta and oxide of lead, chrysophanic acid forms very unstable compounds, which are decomposed even by the carbonic acid in the air. Its alcoholic solution forms with alcoholic subacetate of lead, a reddish-white precipitate, which changes to rose-red by boiling with water; no precipitate with neutral acetate of lead. The ammoniacal solution of chrysophanic acid yields with neutral acetate of lead, a lilac; with alum, a beautiful rose-coloured precipitate. (Thann.)

CHRYSOPRASE. An apple-green or leek-green variety of chalcedony, coloured by nickel.

CHRYSOPRASE EARTH. See PIMELITE.

CHRYSORETIN. A yellow resin obtained from senna-leaves by evaporating the aqueous extract, treating the residue with alcohol, evaporating, dissolving in ether, and again evaporating. It is a mixture of several substances, perhaps containing chrysophanic acid, or a similar acid. (Bley and Diesel, Jahresber. 1848, p. 828.)

CHRYSORHAMNIN. A yellow crystalline substance contained in Persian berries or yellow berries (*graines d'Avignon, Krautz-beeren*), the fruit of *Rhamnus amygdalinus, R. oleoïdes, R. saxatilis, &c.*, especially in the unripe state. According to Kane (Ann. Ch. Phys. [3] viii. 380), it may be extracted from the berries by ether, in which it is easily soluble. It is nearly insoluble in cold water, soluble in alcohol, and contains 58·02 per cent. carbon, and 4·7 hydrogen, whence Kane deduces the formula $C^{23}H^{22}O^{11}$. By boiling with alcohol or water, it is decomposed, yielding another colouring matter, *Xanthorhamnin*, $C^{23}H^{24}O^{11}$, which is soluble in water and alcohol, but insoluble in ether.

Gellatly (Edinb. N. Phil. J. vii. 252), by treating Persian berries with ether, obtained neither chrysorhamnin nor any other characteristic substance; but with alcohol, he obtained a yellow substance crystallising in needles, which appeared to be xanthorhamnin.

According to Bolley (Chem. Soc. Qu. J. xiii. 327), Persian berries yield an abundant extract when treated with *crude ether* (this may perhaps explain the difference between the statements of Kane and Gellatly); and on evaporating the ether, dissolving the residue in alcohol, filtering, and evaporating with addition of water, stellate groups of yellow needles are obtained, which are not altered by repeated solution, boiling, and precipitation. They gave, by analysis of two specimens, 58·87 and 60·239 per cent. carbon, 4·66 and 4·18 hydrogen. The crystals were somewhat soluble in pure ether, sparingly in water, easily in alcohol. The solution gives with neutral acetate of lead, a brick-red precipitate; with nitrate of silver, a blood-red liquid, and afterwards reduced silver. Hence, and from the analysis, Bolley concludes that this substance is quercetin (*q. v.*)

CHRYSOTILE. See SERPENTINE.

CHULARIOSE. Uncrystallisable sugar. (See SUGAR.)

CHUSITE. See OLIVINE.

CHYLE. (Lehmann, *Gmelin's Handbuch*, viii. 216; *Physiological Chemistry*, ii. 281.—Pelouze and Frémy, *Traité*, vi. 162).—Chyle is that portion of the products of digestion which is absorbed by the lacteal vessels terminating in the inner surface of the small intestines, chiefly the jejunum, and thence passing by numerous converging streams into the main trunk of the absorbent system, called the thoracic duct, through which it is gradually poured into the blood of the left subclavian vein, at a short distance before it enters the right side of the heart.

The physical properties of chyle differ according to the nature of the animal to which it belongs, the condition of the animal, whether lately fed or fasting, and the nature of the food which has been taken. Chyle obtained from the thoracic duct during digestion, is an opalescent, milky, yellowish-white or pale red liquid, having a faint, peculiar odour, a somewhat saline and mawkish taste, and very weak alkaline reaction; its specific gravity varies from 1·012 to 1·022. Nine or ten minutes after removal from the vessels, it coagulates; the coagulum, which contracts in from two to four hours, is smaller in bulk compared with the serum than that of blood; it is very soft, easily torn, and sometimes gelatinous. If of a yellow colour, it generally becomes somewhat reddish on exposure to the air, an effect especially observed in the chyle of horses. The serum of chyle, after separation from the coagulum, is never quite clear; it does not usually become turbid when mixed with water; on boiling with water, a milky turbidity appears in the liquid, which, however, generally deposits only a few small clots. Acetic acid often produces a turbidity in the serum, and the filtered liquid when evaporated exhibits on its surface, colourless, transparent films of albuminate of sodium. Ether does not coagulate chyle-serum, but renders it clearer, and between the ether and the serum there is formed a cream-like stratum of a dirty yellowish-white colour.

The chyle of birds, amphibia, and fishes, is nearly transparent and colourless; in horses, it is of a deeper red colour than in any other animals which have been examined with reference to this subject. That of carnivora is comparatively thick and milky; that of herbivora, thinner and more transparent; in cats, it is of a perfectly milky whiteness, whatever may be the nature of their food. During digestion, the chyle is for the most part very turbid; at other times it forms a faintly opalescent fluid, exhibiting a reddish colour only in the thoracic duct.

The morphological elements of the chyle, are: 1. Extremely small granules, consisting of drops of fat enclosed in an albuminous envelope.—2. Granules bound together by a hyaline substance, with or without nuclei, and separate granules with distinct nucleus.—3. The so-called chyle-cells, 0·002 to 0·0055 of a line in diameter, the granules of which mostly become visible on addition of water or acetic acid.—4. The transition forms of the several structures from the more simple to the more complex.—5. A small quantity of coloured blood-cells, especially in the chyle of the thoracic duct.

The *chemical* constituents of chyle are very nearly the same as those of the intercellular fluid of the blood. It is difficult, however, to obtain chyle of constant composition, partly because it varies with the quality and quantity of the food taken, partly because it is always more or less mixed with lymph and blood.

The *fibrin* of chyle is in general less contractile and more gelatinous than that of blood; like the fibrin of many pathological exudations, and that of fish, it sometimes redissolves after coagulation, especially if heated; it is usually destitute of the fibrous structure of blood-fibrin; dissolves very easily in dilute alkalis, carbonic acid, and organic acids; also, after a while, in solution of nitre, and even in sal-ammoniac; from its solution in acetic acid, it is completely precipitated by sal-ammoniac, and from its solution in sal-ammoniac by acetic acid.

The *albumin* of chyle contains a larger amount of alkali than that of blood; it is not rendered turbid, even by very great dilution with water; when boiled, it forms, not coherent flocks, but a milk-white opaque liquid; on evaporation, colourless films form on the surface. The aqueous extract of the chyle-residue has a strong alkaline reaction; on neutralising it with acetic acid, a turbidity is produced, which afterwards redissolves; on subsequently adding ferrocyanide of potassium, a copious precipitate is formed. The original aqueous extract becomes strongly turbid by boiling with sal-ammoniac, also on addition of nitric acid. From chyle-albumin exhausted with water, alcohol, and ether, Lehmann obtained 2·068 per cent. of ash, containing a considerable quantity of alkaline salt which effervesced with acids.

The *fat* of chyle is mostly unsaponified in the smaller lacteals, saponified in the thoracic duct. Chyle does not appear to contain any crystallisable fat.

The existence of *sugar* in chyle is doubtful; that of *bile-constituents*, though probable, has not been demonstrated. *Lactic acid* was found by Lehmann in the chyle of two horses, one of which had been fed two hours before death, with oats, the other with starch.

Chyle is very rich in *alkalis*, combined partly with albumin, partly with lactic and sebacic acids; hence the aqueous solution of the ash has a strong alkaline reaction, and effervesces with acids. *Sulphates of the alkali-metals* are found in the ash, but not in the chyle itself. *Sulphocyanides* are not found. Alkaline phosphates occur in small quantity only, even after the digestion of vegetable food. The *chlorides of sodium* and *potassium* occur in large quantity.

Iron is found in the serum of chyle, but its presence may be due to admixed blood-cells.

During fasting or scanty nutrition, the chyle is poorer in solid constituents, especially fat, and consequently has a turbid but not a milky appearance.

Food rich in fat, whether animal or vegetable, increases the quantity of fat in the chyle.

In the contents of the thoracic duct, two hours after death, of a man killed by drowning, Rees found 98·48 per cent. water, 7·08 albumin, with traces of fibrin, 0·56 aqueous extract, 0·5 alcoholic extract, 0·44 chloride, carbonate, and sulphate of potassium, with traces of phosphate of potassium and oxide of iron, and 0·92 fatty matters.

F. Simon has given the following analyses of the chyle of three horses, the first fed on peas, the other two on oats:

	I.	II.	III.
Water	949·670	928·000	916·000
Fat	1·186	10·010	0·900
Albumin	42·717	46·430	60·530
Fibrin	0·440	0·805	0·900
Hematosin	0·474	trace	5·691
Extractive matter and ptyalin	8·360	5·320	5·265
Chloride and lactate of sodium with traces of calcium-salts	—	7·300	6·700
Sulphate and phosphate of calcium with traces of oxide of iron	—	1·100	0·850
	1002·847	998·965	996·836

The first of these analyses does not, however, admit of direct comparison with the others, as it evidently applies to the organic matter alone.

In the chyle of a cat, Nasse found in 1000 pts.: 905·7 water, and 94·3 solid matter, consisting of 1·3 fibrin, 32·7 fatty matter, 48·9 albumin, globules resembling those of the blood, and extractive matter, 7·1 chloride of sodium, 2·3 other soluble salts, trace of iron, and 2·0 earthy salts.

CHYME. This name, now but little used, was applied to the products of digestion contained in the small intestines, before they have been submitted to the action of the bile and pancreatic juice.

CHYMOSIN. A peculiar nitrogenous matter existing in the gastric juice (*q. v.*); also called *pepsin* or *gasterase.*

CHYTOPHYLLITE. A name applied by Hausmann to certain slags from blast-furnaces, having a broadly laminar structure. They are mainly ferrous silicates, $2Fe^2O.3SiO^2$, the iron being partly replaced by calcium and the silica by alumina. (Jahresber. d. Chem. 1850, pp. 26, 710; 1851, p. 768; 1856, p. 842.)

CHYTOSTILBITE. Radiate blast-furnace slags, having the composition of augite, M^2SiO^3 or $M^2O.SiO^2$, the silica being partly replaced by alumina. (Hausmann, Jahresb. d. Chem. 1856, p. 843.)

CIBOTIUM CUMINGII. An East Indian fern, the hairy stem of which is much used as a means of arresting hæmorrhage. It contains wax, resin, tannic acid, crenic acid, &c. (v. Bemmelen, Viertelj. pr. Pharm. v. 321.)

CICER ARIETINUM. The *Chickpea.*—The hairs of the stem, leaves, and other parts of this plant exude an acid liquid, containing oxalic, acetic, and perhaps malic acid, and, according to Dispan, another acid peculiar to the plant.

CICHORIUM ENDIVIA. See Endive.

CICHORIUM INTYBUS. *Chicory.*—The root of this plant is extensively used for mixing with coffee. The following table exhibits the composition of the organic part of the wild and cultivated varieties, as determined by v. Bibra:

	Cultivated.	Wild.
Fat, insoluble in alcohol	0·07	0·47
Resin	0·84	0·96
Organic acid, precipitable only by subacetate of lead	1·01	1·18
Organic acid, precipitable also by the neutral acetate	2·54	2·51
Sugar	22·08	37·81
Inulin	19·12	10·90
Albumin	0·12	0·15
Tannic acid and volatile oil	trace	trace
Woody fibre	54·21	46·00
	99·99	99·98

The chief difference in the composition of the two varieties appears to be in the relative proportions of inulin and sugar.

Anderson (Highland Agric. Soc. Journ. 1853, p. 61) found in a specimen of chicory cultivated in Yorkshire, 1·6 per cent. nitrogen and 3·6 ash; in another, from the neighbourhood of Glasgow, 1·5 per cent. nitrogen and 6·7 ash.

The leaves contain in 100 pts. 90·9 water and 1·42 ash. (Anderson.)

The composition of the ash of the root and leaves of chicory, as determined by Anderson (*loc. cit.*), and by Graham, Stenhouse, and Campbell (Chem. Soc. Qu. J. ix. 45), is as follows:

Composition of Chicory-Ash *in* 100 pts.

	Root.						Leaves.
	Anderson.		Graham, Stenhouse, and Campbell.				Anderson.
	Scotch.	Yorkshire.	Darkest English (Yorkshire.)	English.	Foreign.	Guernsey.	
Potash . . .	34·6	55·2	37·07	27·13	40·20	41·41	46·6
Soda . . .	8·9	—	8·99	16·46	2·77	4·92	—
Lime . . .	10·1	7·9	10·38	10·53	6·79	6·85	11·3
Magnesia . . .	6·7	4·1	5·83	7·87	4·66	4·97	2·6
Ferric oxide . .	0·8	1·0	4·22	3·41	7·24	4·55	1·0
Silica . . .	4·4	1·3	3·81	2·61	12·75	10·52	0·8
Sulphuric acid (anhydride) . .	15·2	6·2	10·95	11·48	7·32	7·76	7·1
Phosphoric acid (anhydride) . .	16·2	13·0	11·81	12·29	9·60	8·59	7·1
Chloride of potassium	—	2·3	—	—	—	—	1·6
,, sodium .	3·0	8·8	—	—	—	—	1·1
Chlorine . . .	—	—	5·46	5·10	4·39	5·89	—
Carbonic acid (anhydride) . . .	—	—	1·97	3·14	3·81	4·12	20·5
	99·9	99·8	100·49	100·02	99·53	99·58	99·7

When chicory-root is roasted, several volatile products are given off, and on condensing them, a yellowish liquid is obtained, which has a sharp unpleasant odour, colours the skin permanently dark brown, and contains tannic acid. The aqueous infusion of the roasted chicory contains sugar, a bitter substance, empyreumatic oil, substances which exert a strong reducing action on gold and silver-salts, and organic acids precipitable by lead-salts. It has a disagreeable taste, and, if taken in considerable quantity, produces nausea and sometimes giddiness. (Handw. d. Chem. ii. [2] 24.)

CICUTINE. An alkaloïd but little known, said to exist in the water-hemlock, *Cicuta virosa*. (Polex, Arch. Pharm. xviii. 174. — Wittstein, Buchner's Repert. xviii. 19.)

CIDER. A fermented liquor prepared from apples. Large quantities of it are made in Herefordshire, Devonshire, and the adjoining counties; in the counties of Waterford and Cork in Ireland; in Normandy and Picardy in France; in Belgium; in Germany; and in many parts of the United States.

The apples used in the preparation of cider, ripen at different seasons; in this country, the earliest begin to fall from the trees at the end of September, but the majority do not attain their maturity till about the end of November or the beginning of December.

To make good cider, it is necessary that the apples be quite ripe, to ensure which, it is customary to leave them to ripen for a month or more after gathering; they must not, however, be allowed to get over-ripe, otherwise the quantity of sugar will diminish. The average proportion of sugar in apples at different stages of maturity, has been found to be as follows:

Unripe.	Ripe.	Over-ripe.
4·90	11·00	7·95

To make cider, the apples are thrown into a circular stone trough, usually about 18ft. in diameter, called the *chase*, round which the *runner*, a heavy circular stone, is turned by one or sometimes by two horses; the pulpy fruit or "mist" is then enclosed in coarse hair-cloths, and subjected to pressure by a screw-press, and the brown juice which exudes is poured into casks placed either out of doors, or in sheds where there is a free current of air. Sometimes the dry residue which remains in the bags, is mixed with water, ground again, and the liquor pressed out as before. This latter product makes what is called "water-cider," a thin unpalatable liquor which is given to the labourers early in the year.

About three or four days after the juice has been transferred to the casks, it begins to ferment, the thick heavier parts then subsiding to the bottom, while the lighter become clear bright cider. This is then racked off into another cask, and the sediment is put to strain through linen bags, the liquid which oozes through being restored.

The fermentation is the most delicate part of the process; *slight* fermentation leaves the liquor thick and unpalatable; *rapid* fermentation impairs its strength and durabilty; and *excessive* fermentation makes it sour, harsh, and thin. Other things being equal, that cider will probably prove the best in which the vinous fermentation has proceeded slowly, and has not been allowed to pass into the acetous. If the cider does not clear spontaneously, finings, such as isinglass, eggs, or blood, are added, as in the preparation of beer.

At the beginning of January, the cider is moved into cellars, where, by large growers, it is frequently stored in casks of great capacity, containing 1000, 1500, or even 2000 gallons. In March, the liquor is bunged down; it is then fit for sale, and may be used soon afterwards, though it will greatly improve by keeping. For bottled or effervescing cider, the liquor should be bottled or wired down in the September or October after it is made; some persons prefer an earlier time, the end of April or the beginning of May. A more effervescent liquid is thus obtained, but considerable loss occurs from the bursting of bottles. (*Penny Cyclopædia.*)

The strongest cider contains in 100 volumes, 9·87 volumes of alcohol of 92 per cent.; the weakest, 5·21 volumes. (Brande.)

CIMICIC ACID. $C^{15}H^{28}O^{2} = \left.\begin{matrix} C^{15}H^{27}O \\ H \end{matrix}\right\} O$. (Carius, Ann. Ch. Pharm. cxiv. 147.)—An acid, belonging to the oleic series, contained in the fetid oily liquid ejected by a kind of bug (*Rhaphigaster punctipennis*) when irritated. To prepare it, the insects are treated with strong alcohol, which extracts a brown resinous substance, then macerated with cold ether. The solution thus obtained, yields the acid by evaporation, as a coloured mass; it is purified by converting it into a barium-salt, washing with water and with dilute alcohol, then decomposing the salt with hydrochloric acid, and drying the resulting fat between 40° and 50° C. Two or three hundred of the insects yield about 12 grms. of the fatty acid: the insects freed from fat and dried, weighed 23 grms.

Cimicic acid is a yellow crystalline mass, having a peculiar rancid odour: lighter than water and insoluble therein; very little soluble in alcohol, easily in ether, from which it crystallises by slow evaporation in stellate groups of colourless needles. It melts at 44° C., and, when subjected to dry distillation, yields, besides gases, an oil which solidifies on cooling, and appears to contain some undecomposed acid.

Cimicic acid, treated with *pentachloride of phosphorus*, gives off hydrochloric acid gas, and forms a liquid which, when shaken up with cold water, yields chloride of cimicyl, $C^{15}H^{27}O.Cl$, as a heavy oil, which solidifies at about 44° C., does not crystallise distinctly; dissolves in ether without alteration; is immediately decomposed by alcohol into cimicic ether and hydrochloric acid; and by potash into cimicate and chloride of potassium.

Cimicic acid in alcoholic solution is strongly acid. It dissolves easily, with aid of heat, in aqueous alkalis.

The *cimicates* have the composition $C^{15}H^{27}MO^{2}$. Those of the alkali-metals dissolve in a small quantity of water, but a larger quantity renders the solutions opalescent; they froth with soap-solution, and are precipitated from their aqueous solutions by excess of alkali and by chloride of sodium. The cimicates of the earth-metals and heavy metals are nearly or quite insoluble in water and alcohol; the *lead-salt* only appears to be slightly soluble in ether. The *silver-salt* blackens quickly when exposed to light.

Cimicate of Ethyl, $C^{15}H^{2}(C^{27}H^{5})O^{2}$, obtained by treating chloride of cimicyl with with alcohol and precipitating by water, is a light yellow oil, smelling like the free acid, but stronger: it is lighter than water; does not solidify at 0° C; dissolves readily in alcohol; turns brown when heated.

CIMMOL. Syn. with HYDRIDE OF CINNAMYL (p. 988).

CIMMYL. Löwig's name for the radicle $C^{9}H^{7}$, which he supposes to exist in cinnamic acid.

CIMOLITE or **CIMOLIAN EARTH,** the *cimolia* of Pliny, which was used by the ancients both medicinally and for cleaning cloths, and which has been confounded with fuller's earth and tobacco-pipe clay, is found in the island of Argentiera, the ancient Cimolus, also in Bohemia and in Russia. It is of a light greyish-white colour, acquiring superficially a reddish tint by exposure to the air; massive; of an earthy, uneven, more or less slaty fracture; opaque when shaved with a knife, smooth, and of a greasy lustre; tenacious, so as not without difficulty to be powdered or broken; and adhering pretty firmly to the tongue. Its specific gravity is 2·18—2·30. It is immediately penetrated by water, and splits into thin laminæ of a curved slaty form. Triturated with water, it forms a pappy mass; and 100 grains will give to three ounces of water the appearance and consistence of a thickish cream. If left to dry after being thus ground, it detaches itself in hard bands, somewhat flexible, and still more difficult to pulverise than before.

When it is ground with water, and applied to silk or woollen fabrics greased with oil of almonds, the oil is completely discharged by a slight washing in water, after the stuffs have been hung up a day to dry, without the least injury to the beauty of the colour. It is still used by the natives of Argentiera for the same purposes as of old.

The following are analyses of cimolite: —*a.* From Argentiera, by Klaproth: — *b.* From Alexandrowski in Russia, by Ilimoff: — *c.* A pseudomorph of augite (also called *anauxite*), from the decomposed basalt of Bilin, Bohemia, by Rammelsberg: — *d.* Also called *pelikanite*, from the decomposed granite of Kiew in Russia, by Ouchakoff. (*Rammelsberg's Mineralchemie*, p. 583.)

	SiO^2	Al^4O^3	Fe^4O^3	Ca^2O	Mg^2O	K^1O	P^2O^5	H^2O	
a.	63·00	23·00	1·25	—	—	—	—	12·00	= 99·25
b.	63·52	23·55	—	—	—	—	—	12·00	= 99·07
c.	62·30	24·23	—	0·83	—	—	—	12·34	= 99·70
d.	65·66	22·84	0·44	—	0·56	0·30	0·17	9·31	= 99·28

The first three analyses agree nearly with the formula $2Al^4O^3.9SiO^2 + 6aq.$, which is that of a sesquisilicate, and reducible to $2al^2O.3SiO^2 + 2aq.$ or $al^4SiO^4.SiO^2 + 2aq.$; the fourth contains the same proportions of silica and alumina, but only 4 at. water, $2Al^4O^3.9SiO^2 + 4aq.$

Cimolite appears to be formed from augite containing alumina and magnesia, by the action of infiltrating waters containing carbonic acid, which carry away the magnesia, leaving a hydrous silicate of aluminium; an addition of alnmina may probably take place through the accompanying decomposition of associated felspar. (Dana, ii. 164.)

CINACROL. A product of the action of iodine on wormseed oil (*q. v.*)

CINÆBENE and **CINÆBENE-CAMPHOR.** Constituents of wormseed-oil, according to Hirzel.

CINÆPHANE, CINÆPHENE, CINÆPHONE. Products obtained, according to Hirzel, by the action of iodine on wormseed-oil (*q. v.*)

CINCHONA BARK. *Cortex Chinæ, C. Peruvianus, Quinquina, Cascarilla.*— This name is applied to the bark of the stem and branches of various species of *Cinchona* and other genera of the order *Rubiaceæ*, sub-order *Cinchoneæ*. Those which are obtained from trees of the genus *Cinchona*, are called true cinchona barks; they contain quinine and cinchonine, and have long been known for their antifebrile properties; the barks of the other genera of the sub-order above-mentioned, chiefly *Ladenbergia* and *Exostemma*, are called false cinchona barks; they contain certain proximate principles, likewise found in the true cinchona barks, namely quinic acid, quinovic acid, quinotannic acid, and cinchona-red, but no alkaloïds.

The antifebrile barks were first introduced into Europe from Peru, about the year 1638, by the Countess of Chinchon, wife of the Viceroy of Peru (in whose honour the name *Cinchona* was given to the genus by Linnæus), and a few years later by the Jesuits, and soon acquired great celebrity for the cure of intermittent fevers, being known by the names *Pulvis Comitissæ, Jesuiticus, Cardinalis, Patrum.* The trees which yield them were first recognised and described, about a century later, by the French astronomer La Condamine, in his journey in Peru.

The true cinchonas grow on the wooded slopes of the Cordilleras, from western Venezuela to northern Bolivia, between 10° N. and 19° S. latitude, in a narrow zone extending through a vertical height of about 6400 feet. The barks which are richest in alkaloïds, and are exported (*Cascarillo's fino's*), occur most abundantly from 7° N. to 15° S. latitude, and as they require a cool moist climate, they occupy the region from 11,150 to 6400 feet above the sea-level, whilst those which contain smaller quantities of the alkaloïds, and are therefore not fit for exportation, occupy a warmer and drier zone, between 6400 and 4800 feet in vertical height. With these also are found the *Ladenbergias*, which produce false cinchona barks; they extend also 2000 feet lower through the tropical part of the continent. The *Exostemmas*, which also produce false cinchona barks, inhabit only the hot zone, and are found not only on the continent, but on the islands. Since 1853, the most highly prized cinchonas have been successfully cultivated in Java. The cultivation has also been attempted in Algeria and in India.

The collection of the bark takes place in New Granada at all times of the year; in Peru and Bolivia, only in the dry season. The inner bark of the stems and larger branches, after having been freed from the outer bark, is very carefully dried over a fire for three or four weeks, the weight of the dried products being about one-third of that of the fresh bark. According to Karsten, a tree 60 feet high and 5 feet in diameter, yields about 10 cwt. of dry bark; but such specimens are not often met with. In Ecuador and northern Peru, the bark is taken chiefly from the branches; in southern Peru and Bolivia, from both stems and branches; it is dried in the sun, either in the forest itself, or in drier situations lower down the hill-side. According to Pasteur, the process of drying in the sun is injurious.

The TRUE CINCHONA BARKS known in commerce, are of three kinds, *grey* or *brown*, *yellow*, and *red*. They come to market either in rolled quills, or in flat or hollowed oblong pieces of very various dimensions. They have a more or less splintery-fibrous texture, contain the cinchona alkaloïds, quinine, cinchonine, quinidine, &c., and when coarsely powdered and heated in a test-tube, give off a red tar.

a. Grey Cinchona-barks. *China fusca* s. *grisea*.—These barks are obtained from the branches, and have therefore the form of quills; they are whitish on the outside, with spots of grey, greyish-brown or brown, sometimes black, fine-fissured, of even fracture, splintery only on the inner surface, and contain more cinchonine than quinine. Five species are enumerated, namely, *Huanoco*, *Loxa*, *Pseudoloxa*, *Huamalies*, and *pale Jaen bark*.

b. Yellow or Orange-yellow barks. *Cinchona flava* s. *aurantiaca*.—These barks are obtained from the stems and larger branches, and consist wholly or nearly so of the bass or inner bark; hence they have a fibrous or splintery texture. The alkaloïds contained in them are chiefly quinine and quinidine. The most important species is the Royal, King's or Calisaya bark, of which there are three varieties, viz.—1. Fine Calisaya bark, from *C. Calisaya*, which occurs either in quills or rolls, of 1 to 1½ inches diameter, partly covered with the outer bark, and is then called *Cinchona Calisaya tecta* s. *convoluta;* or in flat plates destitute of outer bark; *C. Calisaya nuda* s. *plana;* this last variety is the richest of all the barks in alkaloïds.—2. *C. Calisaya morada*, from *C. Boliviana;* and 3. *C. Calisaya fibrosa* s. *scrobiculata*. There are four other species of yellow bark, viz. *Cusco bark* (Weddell); *Carthagena* or *Bogota bark*, also called *Cinchona flava fibrosa; Cinchona flava dura;* and *Cinchona Pitaya*.

c. Red Barks. *Cinchona rubra*.—These barks are obtained from the stems and larger branches; they are mostly of brown-red colour, with proportionately thick outer bark, and strong fibrous or splintery bass. They contain more quinine than cinchonine. The species are *Cinchona rubra suberosa*, from *C. succirubra* and *C. rubra dura*.

FALSE CINCHONA BARKS are derived chiefly from trees of the genera *Ladenbergia* and *Exostemma*. They occur in rolls, half rolls, or flat pieces, having a pre-eminently corky texture. They contain no cinchona alkaloïds, and when coarsely pulverised and heated in a test-tube, yield nothing but a dirty yellow or brown tar. The species are: 1. *Cinchona de Para*, obtained from a *Ladenbergia*.—2. *Cinchona nova Granatensis*, from *Ladenbergia oblongifolia* or *magnifolia*. Pelletier and Caventou found in it quinovic acid and an alkaloïd; Winckler found quinovic acid and cinchona-bitter; Hlasiwetz found quinic acid, quinovic acid, quino-tannic acid, and cinchona-red.—3. *Cinchona nova Brasiliensis*, from *Ladenbergia Riedelana*, said to contain quinic and quinovic acids.—4. *Cinchona alba Granatensis*, from *L. macrocarpa*, said to contain alkaloïds, but the statement is doubtful.—5. *Cinchona bicolorata* s. *Atacamez*, s. *Pitoya*, said to contain an alkaloïd pitoyine.—6. *Cinchona Caribæa*, from *Exostemma Caribæum*, contains quinovic acid.—7. *Cinchona Sta. Lucia*, s. *Piton*, s. *Martinicensis*, from *Exostemma floribundum*.

The organic constituents of cinchona barks, are quinine, cinchonine, and two or three isomeric modifications of those bases; aricine; quinic, quinovic and quinotannic acids; cinchona-red; a yellow colouring matter; a green fatty matter; a small quantity of volatile oil, having the odour of the bark; together with starch, gum, and woody fibre.

The ash of cinchona barks consists chiefly of carbonate of lime, and varies in quantity from 0·58 per cent. (in Calisaya bark), to 3·4 (in ash-bark or pale Jaen bark). The acids of the bark are neutralised, partly by the lime, partly by the alkaloïds, and accordingly analysis appears to show that the lime diminishes in proportion as the bark is richer in alkaloïds. Some barks, *e.g.* Calisaya and Huanoco, yield ashes of a green colour, arising from manganate of potassium (Puttfarcken, Pharm. J. Trans. xi. 129). Reichel found in the ash of various cinchona barks, potash, lime, magnesia, silica, and sulphuric acid, with smaller quantities of alumina, iron, manganese, phosphoric acid, and chlorine.

The first chemical examination of cinchona bark appears to have been made in 1785 by Hermbstädt, who obtained from it the calcium-salt of quinic acid, which he designated as *essential salt of quinine*. Schneider in 1807 and Vanquelin in 1808, separated quinic acid from the calcium-salt. Quinotannic acid was discovered by Deyeux in 1793, and obtained in more definite form by Séguin, in 1797. Cinchona-bitter and cinchona-red were obtained from red cinchona bark by Reuss in 1810. At this time, ten years before the discovery of the cinchona alkaloïds, Berzelius made a quantitative examination of a yellowish-brown cinchona bark, and found in it 0·5 per cent. of green soft resin, which quickly hardened, 7·35 quinotannic acid, 6·87 bitter syrupy extract (this contained the alkaloïds), 2·5 quinate of potassium and quinate of calcium, coloured by a small quantity of extractive deposit, 1·25 extractive deposit dissolved out by carbonate of potassium, 2·70 amylaceous gum and 73·75 woody fibre.

Cinchonine appears to have been obtained in an impure state by Gomez of Lisbon in 1811; but its true nature remained unknown till 1820, when Houton-Labillardière first drew attention to the alkaline reaction of the substance obtained by Gomez, and communicated his observations to Pelletier and Caventou, who, in the same year, succeeded in isolating, first **cinchonine**, and afterwards **quinine**, and in proving them to be true vegetable alkaloïds. Several isomeric modifications of these alkaloïds were afterwards discovered and variously named; but according to **Pasteur** (Compt. rend. xxxvi. 26; xxxvii. 110), whose results appear to be the most exact, their number may be reduced to four, namely, **cinchonicine** and **cinchonidine** isomeric with cinchonine; **quinicine** and **quinidine** isomeric with quinine. Cinchonicine and quinicine are produced by the action of heat on cinchonine and quinine respectively; cinchonidine is found in certain cinchona barks, namely, Huamalies, Maracaibo, and Bogota barks, and quinidine is obtained from the mother-liquors of the manufacture of sulphate of quinine.

The three isomeric bases of each group are distinguished by their optical rotatory power. (See the several Alkaloïds.)

Aricine was discovered in 1829 by **Pelletier** and **Corriol** (J. Pharm. xv. 575), in a white cinchona bark, from Arica. Elaborate examinations of various cinchona barks, were published by Reichardt in 1855, and by Reichel in 1856; and lastly, in 1860, De Vry published his researches (*Bonplandia*, viii. 270), on the *Cinchona Calysaya* cultivated in Java.

Cinchona barks are employed medicinally in the form of tinctures and infusions, and were used in this manner, for their febrifuge and tonic properties, long before the discovery of the alkaloïds; but as these qualities are likewise possessed by the pure alkaloïds, and the administration of these alkaloïds is, in many cases, much more convenient than that of the bark in substance, the alkaloïds, especially quinine in the form of sulphate, are prepared from the barks on a very large scale;—the value of a bark to the manufacturer may indeed be said to depend on the quantity of sulphate of quinine that it will yield. It is found, however, that the medicinal properties of the barks are due to the quinic and other acids which they contain, as well as to the alkaloïds, and consequently that the bark in substance cannot in all cases be advantageously replaced by the pure alkaloïd. At one time indeed it was supposed that the medicinal efficacy of the barks depended chiefly on the tannin contained in them. Berzelius wrote in 1831 (*Traité de Chimie*, Paris, v. 587): "There is a law in Sweden in virtue of which, every cinchona bark imported into the country must be tested with infusion of galls, ferric sulphate, solution of gelatin, and tartar emetic; and it is proved, by an experience of sixteen years, that the most efficacious bark is that which gives the strongest precipitate with solution of gelatin and tartar-emetic, in other words, which contains most tannin." The barks which appear to be best adapted for medicinal use are, the flat Calisaya and the Huanoco barks, the former containing the largest proportion of quinine and quinotannic acid, while the latter is richest in cinchonine and quinic acid.

Reactions of Cinchona Barks.—The aqueous infusion of these barks contains the alkaloïds in combination with quinic and the other acids,—and as these salts, and likewise the starch, are more soluble in hot than in cold water, the liquid always becomes turbid on cooling. To extract the whole of the bases, it is necessary to acidulate with hydrochloric or sulphuric acid.

The solution thus obtained may be tested:

1. For **alkaloïds**, which, if present, will give a white precipitate with *tannic acid*, and a yellow crystalline precipitate with *dichloride* of platinum. Another mode of testing for the alkaloïds, is to precipitate the acid solution with carbonate of sodium, and distil the precipitate with excess of caustic alkali, whereby a distillate of chinoline (p. 869) will be obtained.

2. For **Quino-tannic acid.**—White precipitate with *solution of gelatin;* green with *ferric salts;* dirty white with *tartar-emetic.*

3. For **Quinovic acid.**—If this acid is present, *sulphate of copper* first colours the liquid green and then throws down a precipitate, which when collected and washed, has a bitter metallic taste. Winckler proposes to estimate the relative value of cinchona barks by the amount of quinovic acid thus precipitated, inasmuch as the bitterness of a bark depends partly (and in the case of the false barks, exclusively) on the presence of quinovic acid.

4. For **Quinic acid.**—This acid distilled with *sulphuric acid and peroxide of man-*

ganese, yields a distillate of quinone, which is a yellow crystallisable substance, having a pungent odour, and soluble in water. The aqueous solution mixed with ammonia, absorbs oxygen from the air, and assumes, first a brown, then a black colour; a reaction which will indicate the presence of very small quantities of quinic acid. Chlorine-water changes the colour of the aqueous solution of quinone from yellow to bright green. The formation of quinone in this manner is proposed by **Stenhouse** (Mem. Chem. Soc. ii. 226), as a means of distinguishing between true and false cinchona barks, the former alone containing quinic acid. According to other authorities, however (p. 964), this acid is likewise present in some of the false cinchonas.

For the *quantitative estimation* of the alkaloïds, the following methods may be used.

1. One drachm of the finely powdered bark is to be boiled for a few minutes with an ounce of water and half a drachm of strong acetic acid; the liquid filtered off, the residue boiled with a little dilute acetic acid; the liquid again filtered off, and the powder washed; the whole of the liquid evaporated to dryness on a water-bath; and the extract dissolved in a little water and again evaporated, to expel all the free acetic acid. The residue is then to be treated with absolute alcohol and blood-charcoal; the colourless solution filtered off, and the residue exhausted with alcohol. To this solution a few drops of hydrochloric acid are to be added, and next a solution of chloride of platinum as long as it causes turbidity; and the precipitate of chloroplatinate of quinine and cinchonine transferred to a weighed filter, washed with alcohol, dried and weighed. The platinum-salt of quinine contains 44·3 per cent. of that base; the cinchonine-salt 43 per cent. of cinchonine: hence the proportion of the two alkaloïds may be found by the method of indirect analysis (p. 224) (**Duflos**). The alkaloïds might also be precipitated by tannic acid and infusion of gall-nuts.

2. Fifty grains of the pulverised bark is treated with a little diluted hydrochloric acid; the liquid filtered, and the residue washed with a mixture of alcohol and a few drops of the same acid. The dark brown solution is then mixed with a little powder of hydrate of lime, so as nearly to decolorise it, and the precipitate, being thrown on a filter, is washed with alcohol. The liquid contains the organic bases in the free state. It is to be neutralised with hydrochloric acid, diluted with water, and freed from alcohol by evaporation. When it is reduced to two or three drachms measure, the bases are to be thrown down with solution of caustic ammonia; and the precipitate is to be filtered, washed with cold water, dried, and weighed. By digesting it with ether, the quinine is dissolved, and the cinchonine remains behind.

As the alcoholic solution of the bases thrown down by the alkali is often rather strongly coloured, and requires to be decolorised by animal charcoal, alum, protochloride of tin, or hydrate of lead, which occasions loss, Thibouwery extracts the alkaloïds from the precipitate by oil of turpentine, or other non-oxygenated oil, and Rabourdin effects the solution by means of chloroform. The same object is attained, according to Badollier and Scharlan, by subjecting the bark, before treating it with acidulated water, to the action of dilute potash, which removes the tannic acid and the cinchona-red.

3. A quarter of a pound of the coarsely powdered bark is boiled for half an hour with very dilute hydrochloric acid; this operation is repeated on the filtered residue; the final residue is washed with water; the whole of the liquors evaporated to dryness over the water-bath; and the extract redissolved in faintly acidulated water, on the bath. Much of the cinchona-red will remain undissolved. The filtrate is to be concentrated to a small bulk, its bases precipitated by ammonia, and the mixture drained and washed with cold water on a weighed filter. The quinine and cinchonine may then be separated and determined, as above, by means of ether.

4. An ounce of the pulverised bark is digested with five ounces of water containing hydrochloric acid (1½ drachm of acid to a pint of water); the extract is pressed through linen, the operation being repeated three times with each four ounces of the acidulated water; the extracts are then evaporated on the water-bath to six ounces, and the residue washed. From this solution, the alkaloïds are precipitated by soda-ley, till an alkaline reaction is produced; the liquid is then supersaturated with acetic acid; and after the cinchona-red has separated, the nearly limpid liquid is to be filtered. The filtrate is again precipitated with soda-ley; the precipitate left to settle for a day; the clear liquid decanted; the precipitate collected on a small filter, and left to drain well; the still moist filter, with the precipitate, repeatedly shaken up with chloroform; the clear chloroform containing the alkaloïds poured into a tared capsule; the operation repeated three times, with fresh chloroform; and the liquid left to evaporate in the capsule: the net weight gives the total amount of the alkaloïds. The quinine may then be completely dissolved out by ether, the residue in the capsule consisting wholly of cinchonine, which may be weighed. In this manner the relative quantities of the two bases are determined.

A crystalline deposit in the amber-like mass of quinine, indicates the presence of isomeric alkaloïds. To separate cinchonidine (Pasteur's, p. 965), dissolve 1 gramme of the mass in 15 drops of dilute sulphuric acid and 24 drops of water, then add 20 drops of ether and 30 drops of ammonia: the quinine will then dissolve, leaving the cinchonidine, provided the quantity of the latter is not less than 10 per cent. Smaller quantities may be separated by means of ether already saturated with cinchonidine, which will still dissolve quinine. (Zimmer.)

Quinidine may be separated from quinine by the greater solubility of its oxalate in cold water; on treating a solution of quinine with oxalate of ammonium, the quinine is almost wholly precipitated as oxalate, whilst the quinidine-salt remains dissolved.

The following table (p. 968) exhibits the proportions of the alkaloïds contained in different cinchona-barks. The determinations must not however be regarded as very exact, partly because the barks known in commerce by the several names in the table are usually mixtures of different sorts, partly also because different methods of analysis often give different results. According to Wittstock, the precipitation of the bases from the acid extract of the bark by alkalis, is not complete, inasmuch as a somewhat considerable precipitate may afterwards be obtained with tannic acid. Moreover, the precipitates which contain the colouring matter always retain a certain portion of the alkaloïds, and charcoal, if used to decolorise the extract, carries down nearly the whole of the bases; lastly, the separation of quinine from cinchonine by ether is by no means complete.

Reichardt has determined the whole of the constituents of various cinchona-barks. The following is an extract from his table:

Composition of CINCHONA-BARKS.

	Cinchona flava fibrosa.	*Cinchona rubra.*	*Cinchona Huanoco.*	*Cinchona Calisaya plana.*	*Cinchona Calisaya convoluta.*
Quinine	0·705	0·955	0·854	2·701	0·659
Cinchonine	0·245	0·389	2·240	0·264	0·327
Ammonia	0·266	0·100	0·086	0·137	0·123
Quinic acid	6·730	6·019	8·985	6·944	7·245
Quinovic acid	0·196	0·222	1·736	0·684	0·679
Quinotannic acid	0·964	3·179	0·515	3·362	2·162
Cinchona-red	0·933	4·384	—	0·722	0·705
Humic acid	7·729	9·933	27·088	16·355	27·345
Cellulose	59·146	47·777	25·429	45·522	32·653
Total of organic constituents	77·604	74·224	68·514	77·968	72·777
Inorganic constituents	1·634	1·661	2·513	1·224	1·650

In the bark of *Cinchona Calisaya*, cultivated in Java, De Vry found ordinary quinine, crystallisable quinine, quinidine, cinchonine, and quinovic acid. The stem-bark was found to contain 3·90 per cent. of quinine and quinidine; the root-bark 1·136 of the crude alkaloïds; the root-wood 0·06, chiefly cinchonine; the stem-wood 0·08, quinine and cinchonine; the young branches scarcely a trace of alkaloïds; the leaves none. Quinovic acid was found more abundantly in the wood than in the bark; in greatest quantity in the root-wood, and least in the leaves. The bark of *Cinchona lucumæfolia*? yielded only 0·4 per cent. of crude alkaloïds. (Handw. d. Chem. ii. [2] 971.)

CINCHONA-RED. A constituent of cinchona bark, produced from quinotannic acid by atmospheric oxidation. It may be extracted by boiling the bark with water, treating the residue with ammonia, and precipitating the ammoniacal filtrate with hydrochloric acid, washing the resulting precipitate of quinovic acid and cinchona-red, and boiling it with thin milk of lime: quinovate of calcium then dissolves, and cinchona-red remains undissolved in combination with lime. The residue, after being washed with water, is treated with hydrochloric acid; then washed again, dissolved in ammonia, and reprecipitated by hydrochloric acid; dissolved in alcohol, after another thorough washing; and the filtrate evaporated to dryness over the water-bath. (Schwarz, Ann. Ch. Pharm. lxxx. 332.)

Cinchona-red is an amorphous, chocolate-coloured or red-brown, nearly black mass, almost insoluble in water, easily soluble, with red-brown colour, in alcohol, ether, and alkaline lyes, also in strong acetic acid. It is decomposed by heat, giving off copious red fumes, and yielding by dry distillation, an empyreumatic oil, pyrogallic acid, and an impure, volatile, carmine-coloured, aromatic substance, insoluble in water, but soluble in alcohol, ether, and alkaline liquids. (Boissenot, J. Pharm. [3] xxv. 199.)

The formula of cinchona-red is $C^8H^7O^{3·5}$, according to Schwarz; $C^7H^8O^3$ according to Boissenot; it is doubtful whether it has ever been obtained pure. The bark of *Cinchona lancifolia* (Mutis) contains, according to Reichel, from 1 to 2·5 per cent. of it; other cinchona barks are said to contain a larger amount.

Percentage of ALKALOÏDS *in* CINCHONA BARKS.

Cinchona regia plana.

Quinine.	Cinchonine.	Authority.
1·75	—	v. Santen.
1·26	—	
0·76	0·06	
2·30	0·08	Thiel.
2·19	—	Stratingh.
2·6	—	
2·3	0·12	Wittstock.
3·72	—	Michælis.
1·24	—	Kirst.
2·13	—	Riegel.
3·22	—	
3·3	—	
2·5	—	
2·14	—	Winckler.
1·74	—	Soubeiran.
2·8	—	Henry.
2·70	0·26	Reichardt.
1·23	0·5	Delondre & Bouchardat
2·38	0·66	

Cinchona Quito flava.

Quinine.	Cinchonine.	Authority.
0·3	2·5	Delondre.

Cinchona regia convoluta.

Quinine.	Cinchonine.	Authority.
0·12	—	v. Santen.
0·68	—	
1·83	0·03	
0·91	0·26	
0·35	—	
2·01	—	Michælis.
2·13	—	Soubeiran.
1·09	—	Kirst & Göbel.
0·78	—	
1·1	0·66	Delondre & Bouchardat
1·5	0·82	
0·69	0·33	Reichardt.

Cinchona flava dura.

Quinine.	Cinchonine.	Authority.
0·03	0·17	Winckler.
0·73	0·56	Kirst.
0·42	0·4	v. Santen.
1·0	0·8	Geiger.

Cinchona Pitaya.

Quinine.	Cinchonine.	Authority.
1·5	0·82	Delondre & Bouchardat
1·86	0·99	

Cinchona rubra.

Quinine.	Cinchonine.	Authority.
1·7	0·8	Pell. & Cav.
0·88	0·91	v. Santen.
0·35	1·26	
0·12	1·95	
0·17	1·17	
0·34	1·04	
0·10	2·39	
0·08	0·26	
0·83	0·41	Michælis.
0·52	0·84	Winckler.
0·10	2·34	
0·08	1·04	
2·65	1·54	Riegel.
0·82	0·73	
2·34	1·3	Duflos.
1·66	1·08	Henry.
1·5	0·82	Delondre & Bouchardat.
1·8	0·99	
1·12	0·4	
1·34	0·5	
0·95	0·38	Reichardt.

Cinchona flava fibrosa.

Quinine.	Cinchonidine.	Cinchonine.	Authority.
0·12	—	0·36	v. Santen.
0·34	—	0·44	
0·34	—	—	
1·00	—	0·90	Geiger.
0·70	—	—	Kirst.
—	—	1·05	Winckler.
2·72	—	0·31	Bidtel.
1·33	—	2·73	
1·03	—	1·89	
2·23	—	0·26	Delondre & Bouchardat
2·38	—	0·33	
0·38	—	0·63	Pereira.
1·4	1·17	—	
0·34	0·15	0·37	Hindsley.
0·77	0·25	1·26	
0·70	—	0·24	Reichardt.

Cinchona rubiginosa.

Quinine.	Cinchonidine.	Cinchonine.	Authority.
—	—	3·0	Franck.
—	—	3·33	Winckler.
—	—	1·01	

Cinchona Huanoco.

Quinine.	Cinchonidine.	Cinchonine.	Authority.
—	—	0·96	v. Santen.
—	—	2·73	
0·4	—	2·5	Stratingh.
—	—	1·58	Wittstock.
0·42	—	0·65	Michælis.
0·36	—	0·96	
—	—	2·18	Kirst.
—	—	2·47	Winckler.
—	—	1·57	Buchner.
—	—	2·8	Böttcher.
—	—	2·4	Riegel.
—	—	1·87	
0·32	—	1·04	Varenton.
0·4	—	1·85	Henry.
1·3	—	3·4	Duflos.
0·24	0·28	1·28	Howard.
0·85	—	2·24	Reichardt.
0·15	—	0·66	Delondre & Bouchardat
—	—	0·82	

Cinchona Huanoco Plana.

Quinine.	Cinchonidine.	Cinchonine.	Authority.
0·45	—	1·0	Delondre.

Cinchona Loxa.

Quinine.	Cinchonidine.	Cinchonine.	Authority.
—	—	0·36	Bucholz.
0·06	—	1·0	Thiel.
0·06	—	0·2	
0·1	—	0·24	Michælis.
0·7	—	—	v. Santen.
0·43	—	0·3	Winckler.
0·6	—	0·5	Delondre.
—	0·57	0·06	Howard.
—	1·05	0·08	

Cinchona Pseudo-Loxa.

Quinine.	Cinchonidine.	Cinchonine.	Authority.
0·4	—	0·28	Howard.
0·5	—	0·9	
0·15	—	0·8	Delondre.

Cinchona Jaen pallida.

Quinine.	Cinchonidine.	Cinchonine.	Authority.
0·05	—	0·21	Geiger.
0·88	—	0·16	Michælis.
1·04	—	0·16	
—	0·61	0·86	Howard.
—	1·2	1·6	

Cinchona Jaen nigricans.

Quinine.	Cinchonidine.	Cinchonine.	Authority.
0·75	0·33	—	Delondre.

Cinchona Huamalies.

Quinine.	Cinchonine.	Authority.
0·5	0·85	Thiel.
0·36	0·63	Michælis.
0·16	—	
—	1·2	v. Santen.
0·37	0·5	Kirst.
—	1·67	Hornemann.
—	1·71	
0·3	0·86	Winckler.
—	0·1	
0·08	0·11	

Cinchona Carabaya.

Quinine.	Cinchonine.	Authority.
0·9	0·33	Delondre & Bouchardat
1·34	0·4	

Cinchona Carthagena rosea.

Quinine.	Cinchonine.	Authority.
1·65	0·4	O. Henry.

Cinchona pseudoregia.

Quinine.	Cinchonine.	Authority.
1·01	0·63	Reichel.

Cinchona Maracaibo.

Quinine.	Cinchonine.	Authority.
0·15	0·82	Delondre & Bouchardat
0·22	0·99	

CINCHONA-TANNIC ACID. Syn. with Quinotannic Acid.

CINCHONETINE. A product of the decomposition of cinchonine by peroxide of lead (p. 974).

CINCHONICINE. $C^{20}H^{24}N^{2}O$. (Pasteur, Compt. rend. xxxvii. 119; Chem. Soc. Qu. J. vi. 273.)—An alkaloïd isomeric with cinchonine, and produced from it under the influence of heat. Any salt of cinchonine may be transformed into the corresponding cinchonicine-salt by heat; but to make the transformation complete and prevent decomposition, the heat must be moderate and the salt must be kept for some time in a resinous state. The change takes place most easily with the sulphate, which, when mixed with a small quantity of water and sulphuric acid, remains melted at a very moderate heat, even after all the water has been expelled, and if kept in this state for three or four hours between 120° and 130° C., is completely converted into sulphate of cinchonicine. Pasteur is of opinion that the resinous state of the fused sulphate is essential to the molecular transformation which takes place. The base may be separated from the sulphate by precipitation with an alkali.

Cinchonicine is nearly insoluble in water, but very soluble in alcohol, whether anhydrous or of ordinary strength. It is very bitter, and is precipitated from its solutions in the form of a liquid resin. It deflects the plane of polarisation to the right. It unites easily with carbonic acid, and separates ammonia from its salts at ordinary temperatures. It possesses febrifuge properties. It is distinguished from cinchonidine by its action on polarised light, and by not being crystallisable; from cinchonine also by the latter property, and by its much greater solubility in alcohol, and greater bitterness.

CINCHONIDINE. $C^{20}H^{24}N^{2}O$, or $C^{19}H^{22}N^{2}O$? (Winckler, Repert. Pharm. [2] xlviii. 384; xlix. 1.—Leers, Ann. Ch. Pharm. lxxii. 147.—Pasteur, Compt. rend. xxxvi. 10; xxxvii. 110; Chem. Soc. Qu. J. vi. 275.—Bussy and Guibourt, J. Pharm. [3] xxii. 401.)—This alkaloïd was discovered by Winckler in a bark resembling the Huamalies cinchona-bark, also in that of Maracaibo. It has likewise been found, accompanied by a small quantity of quinine, in the Bogota cinchona-bark (p. 965). According to Pasteur, it is isomeric with cinchonine, ($C^{20}H^{24}N^{2}O$). The German chemists generally give it the name of *quinidine*.

Preparation.—Cinchonidine is extracted from the barks by the same processes as quinine and cinchonine (pp. 966, 971), and purified by crystallising it several times from alcohol of 90 per cent., till the solution no longer deposits any resinous matter by spontaneous evaporation; then reducing the crystals to fine powder; agitating with ether till the powder no longer exhibits with chlorine-water and ammonia, the peculiar green colouring produced by quinine and quinidine; and finally, recrystallising from alcohol. (See also Zimmer's method of separation, p. 967.)

Properties.—Cinchonidine separates from its alcoholic solution by slow evaporation in anhydrous rhombic prisms, of 94°, hard, with vitreous lustre, and having their faces deeply striated. The same striæ are observed on the faces which replace the obtuse edges of the prism, and the crystals cleave perfectly in the direction of these faces. The prism is modified by two brilliant faces, $\breve{P}\infty$ inclined at an angle of 114° 30′, and resting on the acute edges. The crystals are easily reduced to a perfectly white powder, which becomes electric by friction. They do not taste so bitter as quinine.

Cinchonidine is very sparingly soluble in water, 1 pt. of it dissolving in 2180 pts. of water at 17° C., and in 1858 pts. at 100°. It dissolves in 12 pts. of alcohol of sp. gr. 0·835 at 17°; ether dissolves but little of it, 100 pts. of the solution containing only 0·70 pts. of cinchonidine. (Leers.)

A solution of cinchonidine in absolute alcohol at 13° C., deflects the plane of polarisation of a ray of light strongly to the left; $[\alpha] = -144{\cdot}61°$. (Pasteur.)

According to the analyses of Leers, cinchonidine contains from 76·40 to 76·88 per cent. carbon, 7·70—7·81 hydrogen, and 9·99 nitrogen, whence Leers deduced the formula $C^{19}H^{22}N^{2}O$, requiring 76·60 per cent. C, 7·80 H, and 9·93 N, whereas the formula of cinchonine, $C^{20}H^{24}N^{2}O$, requires 77·9 C, 7·79 H, and 9·09 N. Nevertheless, Pasteur regards cinchonidine as isomeric with cinchonine, inasmuch as it is transformed into cinchonicine by heat, without alteration of weight, in the same manner as cinchonine.

Decompositions.—Cinchonidine melts at 175° C., and solidifies in a crystalline mass on cooling. When strongly heated in contact with the air, it burns with a smoky flame, giving off an odour like that of bitter-almonds or quinine, and leaving a considerable quantity of charcoal. Distilled with hydrate of potassium and a small quantity of water, it yields the same mixture of volatile bases as cinchonine (p. 869). When diffused in fine powder through chlorine-water, it dissolves without perceptible change, even after addition of ammonia.

Commercial cinchonidine is often contaminated with quinidine, the presence of which may be detected either by the green colouring produced by chlorine and ammonia, or by exposing the recently deposited crystals to the air; the crystals of quinidine then effloresce without losing their form, assuming a dull white appearance, while the crystals of cinchonidine retain their transparency.

The *Salts of Cinchonidine* are for the most part more soluble in water than those of quinine; they are very soluble in alcohol, but nearly insoluble in ether. The aqueous solution yields with *alkalis* and their *carbonates*, white pulverulent precipitates, which become crystalline when left at rest; and are insoluble in excess of the reagent. With *phosphate of sodium*, *mercuric chloride*, and *nitrate of silver*, they produce white precipitates; light yellow with *chloride of gold*, orange-yellow with *dichloride of platinum*, and brown with *chloride of palladium*. With *sulphocyanate of ammonium* they yield a white, and with *tannin*, a dirty yellow precipitate.

Hydrochlorates of Cinchonidine.—The neutral salt, $C^{20}H^{24}N^2O.HCl$ (at 100° C.), forms large rhomboïdal prisms, having a vitreous lustre, soluble in 27 pts. of water at 17° C., very soluble in alcohol, nearly insoluble in ether.

	Analysis (mean).	*Calculation.*	
	Leers.	Leers.	Gerhardt.
	At 100° C.	$C^{19}H^{22}N^2O.HCl.aq.$	$C^{20}H^{24}N^2O.HCl.$
Carbon . . .	64·34	64·19	69·67
Hydrogen . .	7·17	7·13	6·97
Chlorine . .	10·05	10·54	10·31

The *acid salt*, $C^{20}H^{24}N^2O.HCl + aq.$, forms large crystals, very soluble in water and in alcohol; after drying over oil of vitriol, they give off 5·8 per cent. water; the calculated quantity for 1 at. is 5·1, according to Leers' formula; 4·5 according to that proposed by Gerhardt.

	Analysis (mean).	*Calculation.*	
	Leers.	Leers.	Gerhardt.
	At 100° C.	$C^{19}H^{22}N^2O.2HCl.$	$C^{20}H^{24}N^2O.HCl.$
Carbon . . .	58·30	57·93	63·32
Hydrogen . .	7·12	6·97	6·33
Chlorine . .	18·98	18·99	18·73

Chloromercurate of Cinchonidine, $C^{20}H^{24}N^2O.2(HCl.HgCl)$? crystallises in shining nacreous scales, sparingly soluble in cold water. Analysis gave 34·77 per cent. C, 4·01 H, 31·9 Hg, and 22·46 Cl, agreeing nearly with $C^{19}H^{22}N^2O.2(HCl.HgCl)$, which requires 34·52 C, 3·83 H, 31·97 Hg, and 22·63 Cl. The formula $C^{20}H^{24}N^2O.2(HCl.HgCl)$ would require 35·8 C, 3·51 H, 29·8 Hg, and 21·18 Cl.

The *chloroplatinate*, $C^{20}H^{24}N^2O.HCl.PtCl^2$? is an orange-coloured precipitate, containing at 110° C. from 27·05 to 27·17 per cent platinum, whence Leers deduces the formula $C^{19}H^{22}N^2O.HCl.PtCl^2 + 2aq.$, requiring 27·04 per cent. Pt, whereas Gerhardt proposes $C^{20}H^{24}N^2O.HCl.PtCl^2$, which requires 27·36 per cent. It is not probable that the salt should retain 2 at. of water at 110° C.

Chlorate of Cinchonidine, obtained by decomposing the neutral sulphate with chlorate of potassium, crystallises from alcohol in long silky prisms, grouped in tufts. It melts at a gentle heat, and decomposes with loud explosion at a higher temperature.

Hydrofluate of Cinchonidine forms silky needles, very soluble in water.

Hyposulphite of Cinchonidine, obtained by precipitating the neutral sulphate with hyposulphite of sodium, crystallises on cooling, in long asbestos-like needles, sparingly soluble in water, easily in alcohol.

Nitrate of Cinchonidine is obtained in mammellated crusts, having the appearance of enamel, and very soluble in water.

Sulphates of Cinchonidine.—The *neutral salt*, $2C^{20}H^{24}N^2O.H^2SO^4$ (at 100° C.), crystallises in long silky needles grouped in stars, neutral to test-paper. One pt. of the salt dissolves in 130 pts. water at 17° C., and in 16 pts. at 100°; it is very soluble in alcohol, nearly insoluble in ether (Leers); it dissolves at mean temperatures in 30—32 pts. absolute alcohol, and in 7 pts. alcohol of 90 per cent. (Bussy and Guibourt.)

Analysis (mean).	*Calculation.*	
Leers.	Leers.	Gerhardt.
At 100° C.	$2C^{19}H^{22}N^2O.H^2SO^4$	$2C^{20}H^{24}N^2O.H^2SO^4$
64·75	65·25	67·20
7·05	6·95	6·72
12·01	12·08	11·20

The *acid sulphate* is obtained by evaporation in vacuo, as a crystalline mass composed of shining asbestos-like needles.

Sulphate of Iodocinchonidine.—Cinchonidine forms with iodine and sulphuric acid, a crystalline salt, which acts upon light in the same manner as the corresponding salts of quinine and cinchonine, also two other salts, one yellow and the other olive-green, which do not exhibit these peculiar optical properties. (W. B. Herapath, Chem. Soc. Qu. J. xi. 130.)

Acetate of Cinchonidine crystallises in long silky needles, which are very sparingly soluble in cold water, and give off part of their acid on drying. The *butyrate* and *valerate* form mammellated crusts, having the odour of the respective acids.

The *citrate* forms small needles, having but little lustre. The *hippurate* crystallises in silky needles, having the aspect of fern-leaves, very soluble in water and alcohol. The *oxalate* separates on cooling in long silky needles, from a mixture of the hot alcoholic solutions of oxalic acid and cinchonidine. The mother-liquor deposits by spontaneous evaporation, dull white, mammellated crusts. The *quinate* crystallises in small needles, very soluble in water and in alcohol. The *neutral tartrate* forms beautiful needles, having a vitreous lustre. The *acid tartrate* forms small nacreous needles, very sparingly soluble in water.

Methyl-cinchonidine, $C^{19}H^{21}(CH^3)N^2O$, or $C^{20}H^{23}(CH^3)N^2O$? (Stahlschmidt, Ann. Ch. Pharm. xc. 218.) The *hydriodate* of this base is obtained by the action of iodide of methyl on cinchonidine. It crystallises in colourless shining needles, containing:

	By Analysis.	*By Calculation.*	
	At 100° C.	$C^{19}H^{21}(CH^3)N^2O.HI$	$C^{20}H^{23}(CH^3)N^2O.HI$.
Carbon . .	53·87	53·76	56·1
Hydrogen .	5·92	5·89	6·0
Iodine . .	29·84	29·87	28·0

Oxide of silver converts it into a basic compound resembling methyl-cinchonine.

CINCHONINE. $C^{20}H^{24}N^2O$, or $C^{40}H^{24}N^2O^2$. (Fourcroy, Ann. Chim. viii. 113; ix. 7.—Vauquelin, *ibid.* lix. 30, 148.—Gomez, Edinb. Med. and Surg. Journal, 1811, Oct. p. 420.—Pfaff, Schw. J. x. 365.—Pelletier and Caventou, Ann. Ch. Phys. xv. 291, 337.—Pelletier and Dumas, *ibid.* xxiv. 169.—Liebig, Ann. Ch. Pharm. xxvi. 49.—Regnault, Ann. Ch. Phys. lxviii. 113.—Gerhardt, Rev. scient. x. 886; *Traité*, iv. 105.—Laurent, Ann. Ch. Phys. [3] xix. 363.—Strecker, Compt. rend. xxxix. 58.)

This alkaloïd exists, together with quinine, in most of the true cinchona-barks, most abundantly in *Cinchona Huanoco*, *C. Huamalies*, *C. rubiginosa*, and *C. flava fibrosa*. (See table, p. 968.)

Preparation.—All methods of extracting the alkaloïds from cinchona-barks consist in treating the bark with a dilute acid, and precipitating the alkaloïds from the acid extract, with lime or carbonate of sodium. The general mode of proceeding is as follows:

The bark, reduced to powder, is boiled for an hour or less with 8 or 10 times its weight of water, acidulated with 10 per cent. of strong sulphuric acid, or better, with 25 per cent. of hydrochloric acid; the decoction is strained through a cloth; and the residue is boiled a second and sometimes a third time, with more and more dilute acid till the marc is completely exhausted. The extracts, after cooling, are mixed with a slight excess of milk of lime, added by small portions, to precipitate the alkaloïds together with the colouring matter. The precipitate is left to drain, and submitted to a gradually increasing pressure, the liquids which run off from the cloths and from the press being collected in a single vessel; they yield after a while a fresh deposit. The pressed cake is now dried, and macerated with alcohol in a closed vessel heated over a water-bath. The strength of the alcohol used depends upon the quality of the bark under treatment. For Calisaya bark, which is very rich in quinine, alcohol of 75 to 80 per cent. is sufficiently strong; but barks which contain a smaller proportion of quinine, require alcohol of 85 to 90 per cent., because cinchonine is much less soluble in weak alcohol than quinine.

If the bark is rich in cinchonine, and the quantity of alcohol used is not too large, the cinchonine is deposited in the crystalline state as the alcoholic extracts cool, and an additional quantity may be obtained by decanting the supernatant liquid, and distilling off half or two-thirds of the alcohol. The quinine remains in the mother-liquor and may be separated in the form of sulphate. (See Quinine.)

If on the other hand the bark contains more quinine than cinchonine, it is best to treat the alcoholic extract with dilute sulphuric acid, and remove the alcohol by distillation. The greater part of the sulphate of quinine then separates in a crystalline mass, the rest, together with the sulphate of cinchonine, remaining in the mother-liquor. By precipitating the two alkaloïds with carbonate of sodium, redissolving in sulphuric acid, and recrystallising, a further separation may be effected; or they may be precipitated by a caustic alkali, and separated by ether, which dissolves the quinine much more readily than the cinchonine (p. 966).

Carbonate of sodium is a better precipitant for the alkaloïds than lime, because they are soluble to a slight extent in lime-water and chloride of calcium.

Oil of turpentine, fixed oils, and chloroform may be used instead of alcohol for dissolving the alkaloïds from the crude precipitate thrown down by lime or soda; and these solvents have the advantage of not taking up so much of the colouring matter as alcohol does (p. 966); but they are better adapted for the preparation of quinine than of cinchonine, which is but sparingly soluble in either of them. (See QUININE.)

Properties.—Cinchonine deposited by slow evaporation of its alcoholic solution, forms colourless, shining, quadrilateral prisms or needles, which are anhydrous. It has a peculiar bitter taste, which however is slow in developing itself, on account of the sparing solubility of the substance. It is insoluble in cold water, and requires for solution 2500 parts of boiling water. In alcohol it is much less soluble than quinine, the solubility increasing however with the strength of the alcohol and the temperature. According to Duflos, strong alcohol dissolves 3 per cent of its weight of cinchonine. It is insoluble in ether, slightly soluble in chloroform, volatile oils and fixed oils.

The solutions of cinchonine have an alkaline reaction, and deflect the plane of polarisation of a luminous ray strongly to the right. An alcoholic solution acidulated with sulphuric acid gives $[\alpha] = + 190 \cdot 40°$; acids produce a temporary decrease of the rotatory power. Cinchonine possesses febrifuge properties, but in a much lower degree than quinine.

The following are the mean results of the analyses of cinchonine by various chemists.

	Calculation.		Liebig.	Regnault.	Gerhardt.	Hlasiwetz.	Laurent.
C^{20} . .	240	77·93	76·36	76·78	77·63	77·97	77·29
N^{24} . .	24	7·79	7·37	7·69	7·98	7·75	7·68
N^2 . .	28	9·09	8·87	9·45	—	—	—
O . .	16	5·19	7·40	6·08	—	—	—
$C^{20}H^{24}N^2O$	308	100·00	100·00	100·00			

Laurent assigned to cinchonine the formula $C^{19}H^{22}N^2O$. According to Schützenberger (Jahresber. d. Chem. 1858, p. 372), the name cinchonine is applied to bases of different constitution; one sample which he analysed yielded numbers agreeing with the formula $C^{19}H^{22}N^2O^2$.

Cinchonine melts at 165° C. forming a colourless liquid, which becomes crystalline on cooling; at a higher temperature, it partly sublimes, exhaling an aromatic odour. According to Hlasiwetz, cinchonine may be sublimed in hydrogen or ammonia gas in the form of shining prisms more than an inch long. Heated with *sulphuric acid and peroxide of lead*, it yields a red substance, cinchonetine, which has not been examined (Marchand, J. Chim. méd. x. 362). Other oxidising agents, *e. g.* nitric acid, permanganate of potassium, and a mixture of sulphuric acid and peroxide of manganese, do not exert much action upon it; neither is it decomposed in a definite manner by emulsin (Hlasiwetz). With *nitrous acid*, it forms a base containing 1 at. oxygen more than cinchonine, and isomeric with quinine, but approaching more nearly to cinchonine in its properties (Schützenberger, Jahresber. f. Chem. 1858, p. 371). It dissolves in *fuming sulphuric acid*, yielding sulpho-cinchonic acid, which forms a soluble barium-salt, $C^{20}H^{22}BaN^2O.SO^4$ (Schützenberger.) With *chlorine* and *bromine*, it forms several substitution-bases, as well as a resinous substance. With *chlorine* and *ammonia*, it does not exhibit the green colouring which is characteristic of quinine. With *iodine* and *iodated potassic iodide* it behaves like quinine. Distilled with *hydrate of potassium*, it yields chinoline, together with several other volatile bases (p. 869).

Beta-cinchonine.—Schwabe (J. Pharm. [3] xxxviii. 389), has obtained from commercial quinoïdine (a product of the alteration by heat of quinine, cinchonine, &c. found in the mother-liquors of the preparation of sulphate of quinine), an alkaloïd isomeric with cinchonine, but differing from it in many properties. This β-cinchonine is contained in the portion of quinoïdine which is sparingly soluble in alcohol; and the sulphate is obtained therefrom by dissolving the substance in dilute acid, precipitating with ammonia, treating the washed precipitate with cold alcohol of specific gravity 0·845, again dissolving it in dilute sulphuric acid, and crystallising. The base separated from the sulphate crystallises from boiling alcohol by spontaneous evaporation in rhombic combinations, $\infty P . \infty \breve{P} \infty . oP$ ($\infty P : \infty P = 119°$). The crystallised as well as the precipitated base is anhydrous, and melts at 150° C. β-cinchonine is more soluble in water, alcohol, ether, and chloroform than ordinary α-cinchonine. The following table gives the quantities of these several solvents required to dissolve 1 pt. of α and β cinchonine, as determined by Schwabe.

	α-Cinchonine.	*β-Cinchonine.*
Water, cold	insoluble	insoluble
Water, hot	2500	scarcely soluble
Alcohol, cold	—	173
Alcohol, hot	30	43
Ether	insoluble	378
Chloroform	40	268

The alcoholic solution of β-cinchonine is dextro-rotatory.

β-cinchonine is precipitated white from the solutions of its salts by caustic or carbonated alkalis, the precipitate being somewhat soluble in excess of the reagent, and disappearing when shaken up with ether. A solution of the base containing tartaric acid is not precipitated by acid carbonate of sodium. A neutral solution of the sulphate mixed with chlorine-water and then carefully with ammonia, exhibits a yellow colour. With ferrocyanide of potassium and chlorine, a red colouring is produced, turning green on addition of ammonia. Quinine-solutions thus treated, exhibit a dark red colour; ordinary cinchonine and quinidine, wine-yellow.

Salts of Cinchonine.—Cinchonine dissolves readily in acids. The salts are bitter and are very much like the corresponding salts of quinine, but for the most part more soluble in water and in alcohol. Ordinary cinchonine forms both acid and neutral salts; β-cinchonine apparently only neutral salts.

ACETATE OF CINCHONINE.—A solution of cinchonine in acetic acid always exhibits an acid reaction, however great may be the excess of cinchonine contained in it; but if concentrated by heat, it deposits on cooling, small sparingly soluble crystals, which exhibit no acid reaction after washing. If the liquid be slowly evaporated to dryness, a gummy mass is obtained, which is decomposed by water into an acid salt which dissolves and a neutral salt which remains at the bottom. (Pelletier and Caventou.)

Acetate of β-Cinchonine forms right-angled four-sided prisms, like those of the sulphate and hydrochlorate. (Schwabe.)

ARSENATE of CINCHONINE.—Very soluble; difficult to crystallise.

CARBONATE OF CINCHONINE.—Cinchonine dissolves in aqueous carbonic acid more easily than in pure water; but the solution does not yield a crystallised carbonate.

CHLORATE of CINCHONINE, $C^{20}H^{24}N^2O.HClO^4$.—White bulky crystalline tufts; melts at a gentle heat, and decomposes with explosion at a higher temperature. (Serullas.)

CHROMATE OF CINCHONINE.—Obtained as a yellow amorphous precipitate, adhering to the glass, but becoming crystalline after a while when a solution of sulphate of cinchonine is mixed with acid chromate of potassium. It is decomposed by water and alcohol. (Elderhorst.)

CYANURATE OF CINCHONINE.—A solution of cinchonine in a boiling saturated solution of cyanuric acid deposits rhomboïdal prisms, sparingly soluble in water, insoluble in alcohol and ether. The salt gives off 17·79 per cent. water at 100° C; and decomposes at 200°, exhaling an odour of bitter almonds. (Elderhorst.)

FERRICYANATE OF CINCHONINE, $C^{20}H^{24}N^2O.3HCy.Fe^2Cy^3 + 2aq$.—Orange-yellow precipitate, obtained by mixing the aqueous solutions of hydrochlorate of cinchonine and ferricyanide of potassium. After drying in the air, it undergoes no alteration at 100° C. (Dollfus, Ann. Ch. Pharm. lxv. 224.)

FERROCYANATE OF CINCHONINE, $C^{20}H^{24}N^2O.4HCy.2FeCy + 2aq$.—Lemon-yellow precipitate produced on mixing the alcoholic solutions of cinchonine and ferrocyanic acid. It is very sparingly soluble in alchol, and when heated, either alone, or with water, is decomposed, yielding hydrocyanic acid and a blue residue (Dollfus). *Ferrocyanate of β-cinchonine* is sparingly soluble and crystallisable. (Schwabe.)

FORMATE OF CINCHONINE.—Very soluble; crystallises from a syrupy solution in silky needles.

GALLOTANNATE OF CINCHONINE.—Yellowish-white powder, very little soluble in cold, more soluble in boiling water, whence it separates in transparent grains on cooling.

HIPPURATE OF CINCHONINE.—Uncrystallisable.

HYDROCHLORATE OF CINCHONINE.—The *neutral salt,* $C^{20}H^{24}N^2O.HCl$, obtained by exactly saturating cinchonine with weak hydrochloric acid; crystallises in transparent shining rhomboïdal prisms; melts at 100° C.; dissolves easily in water and in alcohol, but is insoluble in ether. The aqueous solution possesses dextro-rotatory power; $[\alpha] = +139{\cdot}50^\circ$ (Bouchardat). When subjected to electrolysis, it yields chlorocinchonine, together with chlorine, oxygen, and hydrogen. (Babo.)

Hydrochlorate of β-cinchonine, $C^{20}H^{24}N^2O.HCl + 2aq.$, crystallises apparently in rhombic combinations, $\infty P . \infty \breve{P} \infty . oP$, in which $\infty P : \infty P = 126\frac{1}{2}^\circ$. It dissolves in 22 pts. of cold, 3·2 pts. of hot water; in 1 pt. of cold, ½ pt. of boiling alcohol, and in 550 pts. of ether.

Acid hydrochlorate of cinchonine, $C^{20}H^{24}N^2O.2HCl$, is produced by exposing cinchonine to hydrochloric acid gas, and is obtained crystallised by pouring a slight excess of the acid on cinchonine, and dissolving the product in a mixture of water and alcohol. The solution left to evaporate very slowly in an unclosed bottle, deposits very well-defined rhombic tabular crystals, having the acute angles truncated, $\infty \breve{P} : \infty P = 101^\circ$; $\breve{P} \infty : oP = 137$ to 138°. It is very soluble in water, rather less in alcohol; reddens litmus. The solution is dextro-rotatory.

Chlorine passed into a solution of this salt, forms a deposit of acid hydrochlorate of dichlorocinchonine.

Chloromercurate, $C^{20}H^{24}N^2O.2(HCl.HgCl)$.—On mixing a solution of cinchonine in strong alcohol containing hydrochloric acid with a solution of mercuric chloride also in strong alcohol, the mixture solidifies after a while to a mass of small needles, nearly insoluble in cold water, ordinary alcohol, and ether, moderately soluble in boiling water, and in warm alcohol, easily soluble in strong hydrochloric acid. The salt may be dried at 100° C. without alteration.

Chloroplatinate, $C^{20}H^{24}N^2O.2(HCl.PtCl^2)$.—Light yellow precipitate, obtained by adding dichloride of platinum to a solution of acid hydrochlorate of cinchonine. With an alcoholic solution of cinchonine containing hydrochloric acid, the precipitate is crystalline and nearly white, and dissolves after prolonged boiling with water, the solution as it boils, depositing, first a whitish pulverulent precipitate, afterwards beautiful crystals of a deep orange colour. The salt contains, according to Hlasiwetz, 33·1 per cent. C, 3·6 H, and 27·36 Pt, the formula requiring 33·0 C, 3·3 H, and 27·36 Pt.

Chloroplatinate of β-cinchonine, $C^{20}H^{24}N^2O.HCl.PtCl^2$, crystallises on mixing the alcoholic solutions of its component salts, in rhombic combinations, $\infty P . \infty \breve{P} \infty . oP$, in which $\infty P : \infty P = 119$ (approximately). (Schwabe.)

HYDROCYANATE OF β-CINCHONINE, obtained by precipitation with cyanide of potassium, is amorphous, anhydrous, insoluble in water and alcohol. (Schwabe.)

HYDROFLUATE OF CINCHONINE, $C^{20}H^{24}N^2O.2HF$.—A solution of recently precipitated cinchonine in dilute hydrofluoric acid, deposits colourless prisms when concentrated. The salt crystallises easily from dilute alcohol in rhomboïdal prisms terminated by octahedral faces. After drying at mean temperature, it gives off 2·8 per cent. water at 160° C.; at a high temperature, it acquires a fine purple tint, yields a red sublimate, gives off hydrofluoric acid, and becomes carbonised.

HYDRIODATE OF CINCHONINE, $C^{20}H^{24}N^2O.HI + aq.$ (Regnault.)—Much less soluble than the hydrochlorate. Crystallises easily in nacreous needles. Its solution is precipitated by mercuric chloride and cyanide. *Hydriodate of β-cinchonine* is easily soluble in water and in alcohol. (Schwabe.)

HYPOSULPHATE OF CINCHONINE.—Crystallisable; resembles the quinine-salt (*q.v.*)

HYPOSULPHITE of CINCHONINE.—Obtained by precipitation in small needles; very sparingly soluble in cold water. (Winckler.)

IODATE OF CINCHONINE, $C^{20}H^{24}N^2O.HIO^3$ (at 105° C.).—Long silky fibres, very soluble in water and alcohol. Explodes with violence at 120° C.

NITRATE OF CINCHONINE, $C^{20}H^{24}N^2O.HNO^3 + aq.$ (Regnault.)—Obtained by dissolving cinchonine in dilute nitric acid. If the solution is rather concentrated, part of the nitrate separates in oily globules, which, if covered with water, are converted in a few days into a group of oblique rectangular prisms, very soluble in water. The solution is dextro-rotatory, $[\alpha] = +172·48°$ (Bouchardat). When decomposed by the electro-current (from six Bunsen's cells), it gives off oxygen at the positive pole, mixed after a while with carbonic acid and oxides of nitrogen, and at the negative pole, a mixture of hydrogen and nitrogen containing a little ammonia; in the liquid into which the negative pole dipped, a resinous substance was deposited, and the solution decanted therefrom and distilled with potash, yielded ammonia and oily drops of chinoline. (Babo, J. pr. Chem. lxxii. 73.)

Nitrate of β-cinchonine crystallises slowly, by spontaneous evaporation, in monoclinic or triclinic crystals, which are moderately soluble in water and alcohol, and do not effloresce. (Schwabe.)

OXALATES OF CINCHONINE.—The *neutral oxalate* is a white precipitate, insoluble in cold, slightly soluble in boiling water, very soluble in alcohol, especially if hot, and in oxalate of ammonium. The *acid oxalate* is much more soluble than the neutral salt. *Oxalate of β-cinchonine* is crystallisable. (Schwabe.)

OXALURATE OF CINCHONINE.—Obtained by saturating a boiling solution of parabanic acid with excess of cinchonine. The solution dries up to a yellowish transparent mass, which whitens a little as it assumes the crystalline form. When boiled with hydrochloric acid, it dissolves, producing oxalic acid. (Elderhorst.)

PERCHLORATE OF CINCHONINE, $C^{20}H^{24}N^2O.HClO^4 + aq.$—Obtained by decomposing sulphate of cinchonine with perchlorate of barium. Large rhomboïdal prisms, having a strong lustre, and exhibiting a fine blue and yellow dichroïsm, even in very dilute solutions. Very soluble in water and alcohol. Melts and gives off its water at 160° C. and decomposes with explosion at a higher temperature. The salt dried at 30° C. gives off 3·57 per cent. water at 160° (Boedeker, jun. Ann. Ch. Pharm. lxxi. 59). According to Dauber (*ibid.* 66), the crystals belong to the diclinic system of Naumann (see CRYSTALLOGRAPHY), being rhomboïdal prisms of 125° 47′ and 54° 13′ with perpendicular truncation of the acute edges.

Periodate of Cinchonine.—Very unstable prisms, obtained like the perchlorate. According to Langlois, periodic acid oxidises cinchonine more rapidly than quinine.

Phosphate of Cinchonine.—Very soluble. A solution of cinchonine in phosphoric acid, yields by evaporation, sometimes rudimentary crystals, but more generally amorphous, transparent plates, which gradually become crystalline by contact with water.

Phosphate of β-cinchonine forms crystals nearly a line in length, and apparently oblique-angled. (Schwabe.)

Picrate of Cinchonine.—Yellow pulverulent precipitate, nearly insoluble in water, very soluble in alcohol.

Quinate of Cinchonine.—A strong aqueous solution of cinchonine in quinic acid deposits, when left at rest, sometimes silky needles, sometimes a mammellated mass of small granules. The salt dissolves in half its weight of water at 25° C.: it contains water of crystallisation. From a solution in warm alcohol, it crystallises on cooling in colourless, shining, short, compressed prisms, apparently unalterable either by exposure to the air or by a moderate heat, but becoming completely opaque in course of time. Water dissolves them very readily, but with partial decomposition. Their aqueous solution turns reddened litmus blue, but the alcoholic liquid from which they were deposited, turns blue litmus red.

Sulphates of Cinchonine.—The *neutral sulphate*, $2C^{20}H^{24}N^{2}O.H^{2}SO^{4} + 2\,aq.$, is obtained by exactly saturating cinchonine with dilute sulphuric acid. It forms rhombic prisms of 83° and 97°, generally very short, and having their ends truncated or bevelled: cleavable parallel to the prismatic faces; sometimes hemitropic. They are hard, transparent, and have a vitreous lustre; permanent in the air; melt a little above 100° C. and give off their 2 at. water between 100° and 120°. They dissolve at mean temperatures in 54 pts. water, 6½ pts. alcohol of specific gravity 0·85, and 11½ pts. absolute alcohol; insoluble in ether (Baup). It is but slightly decomposed by the electric current.

Sulphate of cinchonine becomes phosphorescent at 100° C. like sulphate of quinine. At higher temperatures, it melts and then decomposes, yielding a resinous matter of a fine red colour. But if the salt be previously mixed with a little water and sulphuric acid, it remains liquid at a low temperature, even after all the water has been driven off; and if kept in this state for three or four hours at 120° to 130° C. it is completely transformed into sulphate of cinchonicine, only a very small quantity of colouring matter being then produced. (Pasteur, p. 969.)

Sulphate of β-cinchonine, $2C^{20}H^{24}N^{2}O.H^{2}SO^{4} + 2\,aq.$—Crystallises in rhombic combinations $\infty P . \infty \breve{P} \infty . o P$, in which $\infty P : \infty P = 136°$. It dissolves in 75 pts. of cold, and 14 pts. of hot water; in 13·6 pts. of cold, and 1·5 pts. hot alcohol of 80 per cent., and is insoluble in ether. The dilute aqueous solution is strongly iridiscent. (Schwabe.)

Acid Sulphate of Cinchonine, $C^{20}H^{24}N^{2}O.H^{2}SO^{4} + 3\,aq.$—By adding sulphuric acid to the neutral sulphate, and evaporating till a slight pellicle is formed, the acid salt is obtained in rhombic octahedrons, often having some of their edges or summits modified, and cleaving very easily, at right angles to the axis, in well-defined shining laminæ. It is permanent in the air at ordinary temperatures, but effloresces in very dry air or if slightly warmed. When heated, it gives off 11·73 per cent. water = 3 at. At 14° C., 100 pts. of the salt [?anhydrous or hydrated], dissolve in 45 pts. water, in 90 pts. of alcohol, of specific gravity 0·85, and in 100 pts. of absolute alcohol: it is insoluble in ether. (Baup, Ann. Ch. Phys. [3] xxvii. 323.)

Sulphocyanate of Cinchonine, $C^{20}H^{24}N^{2}O.HCyS$, crystallises in brilliant anhydrous needles (Dollfus). *Sulphocyanate of β-cinchonine* is also crystallisable. (Schwabe.)

Tartrates of Cinchonine. (Pasteur, Ann. Ch. Phys. [3] xxxviii. 456, 469.—Arppe, J. pr. Chem. liii. 331.)—These salts, neutral and acid, dextro- or lævo-rotatory, are prepared by dissolving cinchonine in the proper proportions in the two modifications of tartaric acid.

α. *Neutral*, $2C^{20}H^{24}N^{2}O.C^{4}H^{6}O^{6} + 2\,aq.$—Large needles grouped in bundles, sparingly soluble in water, and giving off their crystallisation-water, 4·6 per cent., between 100° and 120° C. (Arppe.)

β. *Acid Tartrates.*—The *dextro-rotatory salt*, $C^{20}H^{24}N^{2}O.C^{4}H^{6}O^{6} + 4\,aq.$, forms nacreous shining crystals grouped in radiate stars. They belong to the trimetric system, and are often hemihedral. Observed combination, $\infty P . \breve{P} \infty . P$. Inclination of faces, $\infty P : \infty P = 133° 20'$ (nearly); $\breve{P} \infty : \breve{P} \infty = 127° 40'$; $\frac{P}{2} : \breve{P} \infty = 151° 13'$. The faces ∞P are longitudinally striated. It gives off its water (13·75 – 14·0 per cent.: calculation, 13·58 per cent.) at 100° C., and at 120°, assumes a red colour and begins to melt. It dissolves but sparingly in cold, much more easily in hot water, still more in alcohol; the solution is neutral to test-paper.

A solution containing twice the quantity of tartaric acid required to form this salt, deposits at first, another acid tartrate in transparent well-defined crystals.

Lævo-rotatory acid tartrate, $C^{20}H^{24}N^2O.C^4H^6O^6 + aq.$—This salt gives off its water = 4·58 per cent. (calc. 3·78), at 100° C. It is very sparingly soluble in alcohol and in water; the alcoholic solution is neutral, the aqueous solution acid to test-paper.

If a great excess of acid is used in the preparation, another acid tartrate is obtained crystallised in brilliant tufts, composed of very slender needles, and very different in appearance from the second dextro-rotatory acid tartrate above-mentioned. (Pasteur.)

Urate of Cinchonine, $C^{20}H^{24}N^2O.C^5H^4N^4O^3 + 4\ aq.$—Obtained by boiling uric acid with cinchonine recently precipitated and diffused through a large quantity of water. The liquid filtered at the boiling heat, deposits long prisms sparingly soluble in water, boiling alcohol, and ether. On heating the salt to 100° C. or leaving it to evaporate over oil of vitriol, it becomes opaque, and finally assumes a sulphur-yellow colour, giving off 12·49 per cent. (calc. 4 at. = 13·73 per cent.). During the desiccation, it is in a state of constant agitation, and is finally converted into a crystalline powder, probably differing in form from the hydrated crystals. (Elderhorst, *loc. cit.*)

Brominated, Chlorinated, and Iodated Derivatives of Cinchonine.

Bromocinchonine, $C^{20}H^{23}BrN^2O$. (Laurent, Ann. Ch. Phys. [3] xxiv. 302.)—When bromine is poured upon moist acid hydrochlorate of cinchonine, a product is obtained, which, when freed from excess of bromine by washing with a little alcohol, is a mixture of acid hydrobromate or hydrochlorate of bromocinchonine and sesquibromocinchonine. On treating it with boiling alcohol, the former of these salts dissolves, while the latter is nearly insoluble; and on adding ammonia to the decanted solution, boiling to expel part of the alcohol, and leaving it to cool, bromocinchonine is deposited in laminæ, which may be purified by recrystallisation.

The *acid hydrochlorate*, $C^{20}H^{23}BrN^2O.2HCl$, crystallises in the same form as the corresponding salt of cinchonine. The *chloroplatinate*, $C^{20}H^{23}BrN^2O.2(HCl.PtCl^2)$, is a pale yellow powder, containing at 50° C. 24·2 per cent. platinum (calc. 24·75).

Sesquibromocinchonine, $C^{20}H^{22\cdot5}Br^{1\cdot5}N^2O$. (Laurent, *loc. cit.*)—When the pulverulent residue, insoluble in boiling alcohol, obtained in the preparation just described, is boiled with water, and ammonia added, a white bulky precipitate of sesquibromocinchonine is formed, which, after washing and drying, dissolves in boiling alcohol, and crystallises therefrom in slender needles. It is slightly bitter; its alcoholic solution turns reddened litmus blue. It melts when heated, afterwards blackens with intumescence. It gives by analysis 55·45 per cent. C, 5·18 H, and 28·3 Br, the formula requiring 56·27 C, 5·27 H, and 28·13 Br.

The *acid hydrochlorate*, $C^{20}H^{22\cdot5}Br^{1\cdot5}N^2O.2HCl$, forms rhombic tables, in which $\infty P : \infty P = 107°$ to 108°.

The *hydrobromochlorate*, $C^{20}H^{22\cdot5}Br^{1\cdot5}N^2O.HCl.HBr$, is obtained by pouring bromine on hydrochlorate of cinchonine; boiling with alcohol as above, to remove hydrochlorate of bromocinchonine; again pouring alcohol on the residual salt; boiling; adding ammonia, which dissolves it immediately; then adding excess of hydrochloric acid to the solution, and leaving it to cool. The salt is then deposited in small rhombic tables, in which $\infty P : \infty P = 107°$ to 108°.

The *choroplatinate*, $C^{20}H^{22\cdot5}Br^{1\cdot5}N^2O.2(HCl.PtCl^2)$, is a very pale-yellow precipitate, containing at 100° C. 23·0 per cent. platinum; by calculation, 23·5.

Dibromocinchonine, $C^{20}H^{22}Br^2N^2O$. (Laurent, Compt. chim. 1849, p. 311.)—Bromine in excess is poured on acid hydrochlorate of cinchonine, to which a little water has been added; the product is heated when the action is over, to complete the bromination of the cinchonine, and expel excess of bromine; water is then poured upon it; the liquid is boiled and filtered; alcohol is added to the aqueous filtrate, heat again applied, and the solution is neutralised with ammonia. On cooling, it deposits dibromocinchonine in colourless laminæ, with nacreous reflexion.

Dibromocinchonine is insoluble in water, sparingly soluble in boiling alcohol. At about 200° C. it swells, blackens, and yields a substance which dissolves easily in potash, and is separated therefrom by acids in brown flakes. Dibromocinchonine gives by analysis 51·20 per cent. C, 4·4 H, and 34·00 Br, the formula requiring 51·28 C, 4·70 H, and 34·19 Br. A solution which had been left for some days in an open vessel, deposited rectangular octahedrons, containing 4·2 per cent. = 1 at. water of crystallisation.

The *acid hydrochlorate*, $C^{20}H^{22}Br^2N^2O.2HCl$, obtained by treating the base with hydrochloric acid, is sparingly soluble in water, and separates from a boiling solution on cooling, in rhombic tablets, having their four acute angles truncated; $\infty P : \infty P =$

104° to 105° : $\breve{P}\infty : oP = 137$. Its solution deflects the plane of polarisation to the right.

DICHLOROCINCHONINE, $C^{20}H^{22}Cl^2N^2O$. (Laurent, Ann. Ch. Phys. [3] xxiv. 302.)—The acid hydrochlorate of this base is formed by passing chlorine into a hot concentrated solution of acid hydrochlorate of cinchonine; and on adding ammonia to a solution of this salt in boiling water, the base is precipitated as a light flocculent mass, which crystallises from boiling alcohol in microscopic needles, yielding by analysis 18·9 per cent. chlorine (calc. 18·83).

The *acid hydrochlorate*, $C^{20}H^{22}Cl^2N^2O.2HCl$, is sparingly soluble in water, and requires 50 pts. of alcohol to dissolve it: the solution is dextro-rotatory. The salt crystallises in rhombic tables isomorphous with the crystals of acid hydrochlorate of cinchonine, $\infty P : \infty P = 106°$; $P\infty : oP = 136° 30'$ to $137° 30'$.

The *chloroplatinate*, $C^{20}H^{22}Cl^2N^2O.2(HCl.PtCl^2)$, is a pale yellow powder, yielding at 100°, 25·00 per cent. platinum (calc. 25·06).

The *acid hydrobromate*, $C^{20}H^{22}Cl^2N^2O.2HBr$, obtained by treating the base with hydrobromic acid, is sparingly soluble, and crystallises in brilliant laminæ, having sensibly the same angles as those of the acid hydrochlorate, but presenting a different appearance, inasmuch as the modifying faces are considerably developed, so that the rhombic tablet is transformed into a six-sided prism; $\infty P : \infty \breve{P} = 104°$; $\breve{P}\infty : oP = 137°$. The salt has the same composition as the acid hydrochlorate of dibromocinchonine, but differs from it in giving with nitrate of silver a precipitate of bromide of silver, whereas the latter yields a precipitate of chloride.

The *nitrate* is sparingly soluble in water, and crystallises in small elongated tetrahedrons, formed of four equal scalene triangles, and having their opposite edges truncated.

IODOCINCHONINE, $2C^{20}H^{24}N^2O.I^3$ (?) (Pelletier, Ann. Ch. Phys. [2] lxiii. 181.)—When cinchonine is triturated with about half its weight of iodine, and the product is treated with alcohol of 36 per cent., the whole dissolves, and on leaving the solution to evaporate, it first deposits the so-called iodocinchonine in saffron-coloured plates, afterwards crystalline nodules of hydriodate of cinchonine. On treating the whole with boiling water, the hydriodate dissolves, and the iodocinchonine separates in the melted state.

Iodocinchonine has a deep saffron-yellow colour when seen in mass; its powder is lighter. It has a slightly bitter taste. When heated, it softens at 25° C. but does not enter into complete fusion till heated to 80°. It is insoluble in cold water, very soluble in boiling water, soluble in alcohol and ether. It gave by analysis 28·83 per cent. iodine (calc. 29·03).

Iodocinchonine may be decomposed by the successive action of acid and alkaline solutions. It is likewise decomposed by nitrate of silver. (Pelletier.)

If the preceding formula be correct, the compound is not iodocinchonine, but iodide of cinchonine.

Sulphate of Iodocinchonine. (W. B. Herapath, Chem. Soc. Qu. J. xi. 151.)—Cinchonine treated with iodine and strong sulphuric acid, yields a crystalline salt, which resembles the corresponding quinine-compound in its action on light. It crystallises in long needles, which appear deep purple-red by transmitted, and dark purple-blue by reflected light; their laminæ appear lemon-yellow by transmitted light, and if two such thin plates be superposed in such a manner that their longest dimensions may cross one another at right angles, the system is perfectly impervious to light, the two plates acting in fact like two tourmalines with their axes crossed. (For further details relating to these properties, see SULPHATE OF IODOQUININE, under QUININE). The salt dissolves easily in strong boiling alcohol, and crystallises therefrom; sparingly in weak alcohol, and scarcely at all in water, ether, and chloroform. Herapath assigns to it the formula $C^{30}H^{36}N^4O^2I^6.H^2SO^4 + 3aq.$, which is very improbable.

Sulphate of Iodo-β-cinchonine is obtained in indistinct crystals on adding a warm solution of 3 pts. iodine in 115 pts. alcohol to a solution of 10 pts. of sulphate of β-cinchonine in 144 pts. acetic acid, and 12 pts. dilute sulphuric acid. (Schwabe.)

Derivatives of Cinchonine containing Organic Radicles.

BENZOYL-CINCHONINE, $C^{27}H^{28}N^2O = C^{20}H^{23}(C^7H^5O)N^2O$. (Schützenberger, Ann. Ch. Pharm. cviii. 351.)—Dry cinchonine dissolves with rise of temperature in chloride of benzoyl, and the mixture, if heated for a few seconds, solidifies to a crystalline mass of hydrochlorate of benzoyl-cinchonine. This salt dissolves readily in water, and the solution, quickly decanted from undissolved chloride of benzoyl, yields with ammonia a white glutinous precipitate of benzoyl-cinchonine, which hardens in the cold. It is tasteless and uncrystallisable, insoluble in water, but dissolves in all proportions in alcohol and ether. Its salts are easily soluble in water. The *hydrochlorate* is $C^{27}H^{30}N^2O.HCl$; the *chloroplatinate* $C^{27}H^{30}N^2O^2. 2(HCl.PtCl^2)$.

METHYL-CINCHONINE, $C^{21}H^{26}N^2O = C^{20}H^{23}(CH^3)N^2O$. (Stahlschmidt, Ann. Ch. Pharm. xc. 218.)—The *hydriodate* of this base, $C^{21}H^{26}N^2O.HI$, is produced by the action of iodide of methyl on pulverised cinchonine. It dissolves easily in boiling water, and separates in fine needles on cooling. It is not attacked by iodide of methyl when heated therewith to 100° C. in a sealed tube: hence cinchonine appears to contain but 1 at. of hydrogen replaceable by an alcohol-radicle.

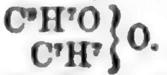
The iodide treated with oxide of silver, yields a solution of the base, which, when quickly evaporated over the water-bath, leaves a brown crystalline mass, from which, when dissolved in water, brown oily drops separate. The aqueous solution precipitates the salts of sesquioxides.

The salts of methyl-cinchonine are very soluble in water and in alcohol, and difficult to crystallise.

The *chloroplatinate*, $C^{21}H^{26}N^2O.2(HCl.PtCl^2)$, yields when dried at 100°C., 26·70 — 26·77 per cent. platinum, the formula requiring 26·93.

CINCHOVATINE. Syn. with ARICINE (p. 357).

CINNABAR. Protosulphide of mercury. (See MERCURY.)



CINNAMEIN. *Cinnamate of Benzyl.* $C^{16}H^{14}O^2 = \left.\begin{matrix} C^9H^7O \\ C^7H^7 \end{matrix}\right\}O$. (Plantamour, Ann. Ch. Pharm. xxvii. 329; xxx. 241.—Frémy, Ann. Ch. Phys. lxx. 189.—H. Deville, Ann. Ch. Pharm. lxxiv. 230.—E. Kopp, Compt. chim. 1850, p. 410.—Scharling, Ann. Ch. Pharm. xcvii. 184.—Gm. xiii. 283.—Gerh. iii. 404.)—This compound was discovered by Plantamour (1838), who obtained it from balsam of Peru, in which, according to Simon, it exists ready formed; according to Frémy and Deville, it exists also in small quantity in Tolu balsam. According to Scharling, cinnamic acid dissolved in peruvin (a mixture of benzylic alcohol and toluene) forms a liquid, which, when saturated with hydrochloric acid, yields to boiling water a neutral oil resembling cinnamein.

Preparation.—Balsam of Peru is saponified by agitation with excess of caustic potash, and the solid soap dissolved in water: the solution on being warmed, separates after a few minutes into two layers, and the upper, which is oily, is to be repeatedly washed with water, till the oil exhibits a faint reddish-yellow colour. The residual water is evaporated over the water-bath; the oil dissolved in warm alcohol and evaporated; and this treatment repeated as long as resin separates out on evaporation. (Plantamour).—2. Balsam of Peru dissolved in alcohol of 36°, is treated with alcoholic potash, whereby a compound of resin with potash is precipitated; the solution is mixed with water; the cinnamein which separates out in the form of an oil is separated from the inferior solution of cinnamate of potassium, and dissolved in freshly-rectified rock-oil, whereby resin is removed; the rock-oil is then evaporated, and the residual oil placed in a vacuum. Cinnamein thus prepared, still retains styracin in solution, the quantity varying according to the nature of the balsam. To free it from this impurity, it is dissolved in weak alcohol, and cooled for several days below 0°, as long as a crystalline deposit of styracin continues to form (Frémy).—3. Balsam of Peru is repeatedly boiled with aqueous carbonate of sodium, and the cinnamate of sodium is removed by washing, the residue then separating into a resin, and a yellowish-brown liquid which must be heated to 170° C. on the oil-bath, and distilled in steam heated to 170°. Colourless, somewhat milky cinnamein then passes over, and is freed from adhering water by standing for some time in a warm place, over chloride of calcium. Sometimes, perhaps always, the cinnamein thus prepared contains in solution styracin, which, after long standing, partially crystallises out (Scharling). Calcined magnesia or oxide of lead also separates cinnamein from balsam of Peru, by combining with the cinnamic acid, and separating resin. (Simon.)

Properties.—Cinnamein is a feebly coloured or colourless, strongly refracting neutral oil, which remains liquid when cooled to −12° or −15° C. for several days. It boils at 305°, and distils without decomposition (Plantamour); between 340° and 350°, with partial decomposition (Deville, Frémy). It has a feeble pleasant odour. Its taste is sharp and aromatic, recalling that of fat. It makes grease spots on paper. Specific gravity, 1·098 at 14°; 1·0925 at 25° (Scharling). It is nearly insoluble in water, but dissolves in alcohol and ether.

Cinnamein contains, according to Scharling's analysis, 79·18 to 79·24 per cent. C, 6·56 to 6·03 H, and 14·26 to 13·72 O, agreeing nearly with the preceding formula, which requires 80·62 C, 5·88 H, and 13·45 O.—When kept under water for some time, it yields a crystalline substance of the same composition, metacinnamein, which melts between 12 and 15° C. sometimes resolidifies after cooling and standing, but after solution in boiling alcohol cannot again be obtained in the crystalline form. (Scharling.)

Cinnamein slowly absorbs moist *oxygen* (**Frémy**). When exposed for years to *air* and *light*, it acquires a rancid odour and acid reaction. Crystallised cinnamein preserved in a glass vessel for a year melted to a viscous mass, and in another year solidified to a transparent amorphous mass (**Scharling**). Cinnamein is partially decomposed by distillation, leaving a small quantity of tar, and yielding a distillate differing in composition from the original substance.

It is resinised by strong *sulphuric acid* (**Frémy**. It slowly absorbs *chlorine*, more easily when heated, becoming at the same time coloured and thickened, and when distilled, ultimately yields chloride of benzoyl together with an oil (**Frémy**). *Nitric acid* acts briskly on cinnamein when heated, forming a yellow resin and a large quantity of bitter almond oil. *Peroxide of lead* acts in a similar manner (**Frémy**). Cinnamein forms a crystalline compound with *ammonia* (**Plantamour**). Mixed with *sulphide of carbon* and powdered hydrate of potassium, it forms a saline mass containing xanthate of potassium (**Scharling**). Rapidly heated with very concentrated *potash-ley*, or melted with hydrate of potash, it gives off hydrogen, and passes into cinnamate (and benzoate) of potassium (**Frémy**). Treated with very concentrated potash-ley in the cold, or with alcoholic potash, it is completely resolved, in 24 hours, without disengagement of gas or absorption of oxygen, into benzylic alcohol and cinnamate of potassium: $C^{16}H^{14}O^2 + KHO = C^7H^8O + C^9H^7KO^2$. By the continued action of the potash, the benzylic alcohol may be converted into benzylene. (C^7H^6.)

Plantamour, by treating cinnamein with strong alcoholic potash, obtained, together with cinnamic acid, an acid which he designated as *carbobenzoic* or *myroxylic acid;* probably impure benzoic-acid resulting from the decomposition of cinnamic acid under the influence of potash (p. 984).

CINNAMENE. C^8H^8. *Cinnamol. Styrol. Volatile Oil of Liquid Storax.* (**Bonastre**, J. Pharm. xvii. 338.—**D'Arcet**, Ann. Ch. Phys. lxvi. 110.—**Mulder**, J. pr. Chem. xv. 307.—**E. Simon**, Ann. Ch. Pharm. xxxi. 265.—**C. Herzog**, Pharm. Centr. 1839, p. 833.—**Gerhardt and Cahours**, Ann. Ch. Phys. [3] i. 96.—**E. Kopp**, Compt. chim. 1846, p. 87; further, Compt. rend. liii. 634.—**Blyth and Hofmann**, Ann. Ch. Pharm. liii. 293, 325.—**Hempels**, *ibid.* lix. 316.—**Scharling**, *ibid.* xcvii. 184.—**D. Howard**, Chem. Soc. Qu. J. xiii. 134; **Gm.** xiii. 1; **Gerh.** iii. 374.)—This compound is produced by the decomposition of cinnamic acid (p. 981), and is contained in liquid storax (p. 982), whence it may be obtained by distillation with water. It was formerly supposed that cinnamene obtained from cinnamic acid was not identical, but only isomeric, with styrol, the volatile oil of storax, because the latter is completely converted by heat into a solid substance, *metastyrol*, of the same composition, whereas with cinnamene this change had been observed to take place but imperfectly; but E. Kopp has lately shown that this transformation takes place quite as completely with cinnamene as with styrol, an observation which removes the only objection to the supposed identity of the two substances.

Preparation.—a. *From Cinnamic Acid and the Cinnamates.* Cinnamic acid, when slowly distilled at its boiling point, is completely resolved into cinnamene and carbonic anhydride:

$$C^9H^8O^2 = CO^2 + C^8H^8.$$

Pure cinnamate of calcium is likewise resolved by dry distillation into cinnamene and carbonate of calcium (**D. Howard**). Cinnamic acid distilled with excess of lime or baryta yields a mixture of cinnamene and benzene, which may be separated by rectification.

b. *From Storax.*—The liquid balsam is distilled in a copper still connected with a worm-tub, with water containing carbonate of sodium, to retain cinnamic acid; 3½ lbs. of carbonate of sodium suffice for 10 lbs. of storax. The water which passes over is milky, and the cinnamene floats on the surface. The quantity obtained varies with the age of the balsam. Blyth and Hofmann obtained in one operation about 360 grammes of oil from 20½ kil. of liquid storax, in another not more than 90 grms. from 13½ kil. The oily distillate is dried over chloride of calcium and rectified. This last operation requires particular precautions. The liquid begins to give off vapour between 100° and 120° C., and at 145° it is in full ebullition, a limpid oil then passing over, and the thermometer remaining stationary for some time; suddenly, however, a considerable rise takes place, and the thermometer must then be quickly withdrawn from the retort, for the residue thickens, and on cooling solidifies to a transparent glass, consisting of metacinnamene or metastyrol. The quantity of this solid residue varies, but it sometimes amounts to half the oil subjected to distillation.

c. Cinnamene may also be obtained from the resin of Peru balsam, by heating that substance mixed with pumice to dull redness in a retort, and subjecting the oil which passes over, together with benzoic acid and an aqueous liquid, to fractional distillation. The portion which goes over under 175° C., and is lighter than water, is collected, repeatedly distilled with potash-solution, allowed to stand several days over pieces of solid potash, and then distilled at a temperature not exceeding 150° C. The distillate is dried with chloride of calcium, treated with potassium, whereby hydrogen is evolved, and the fluid part is decanted from the resulting gelatinous precipitate and distilled. The boiling point then gradually rises to 100°—140° C., by which time all the cinnamene remains behind, amounting to $\frac{3}{8}$ of the liquid employed. (Scharling, Ann. Ch. Pharm. xcvii. 184.)

Cinnamene is a very mobile colourless oil, having a strong persistent aromatic odour, reminding of benzene and naphthalene together. It does not solidify at −20° C. It is very volatile, the grease spots which it produces on paper disappearing in a few seconds. Specific gravity 0·924. Boiling point 145·75° C. (Blyth and Hofmann); 145° (E. Kopp). It is neutral, mixes in all proportions with alcohol and ether, volatile oils, and sulphide of carbon, and dissolves sulphur and phosphorus.

Cinnamene is not acted upon by *potash.* With *fuming sulphuric acid* it appears to form a conjugated acid. If added by drops to *fuming nitric acid,* it dissolves with evolution of red vapours; and water added to the solution throws down a yellow resin, which, by careful distillation, yields crystals of nitrocinnamene. If boiled with excess of nitric acid, it yields benzoic or nitrobenzoic acid, according to the strength of the nitric acid. Distilled with dilute *chromic acid,* it yields crystals of benzoic acid With *chlorine* and *bromine,* it forms chloride and bromide of cinnamene.

Metacinnamene. *Metastyrol. Draconyl.*—This is the solid substance into which cinnamene or styrol is converted by the action of heat. The conversion takes place readily in a sealed tube heated to 200° C. in an oil-bath. Metacinnamene is likewise obtained from dragon's blood. When the crude oil produced by the dry distillation of that substance is distilled till the temperature rises to 280° C. a liquid is obtained containing toluene (hydride of benzyl, p. 573), and cinnamene. On distilling this mixture at a temperature below the boiling point, till the greater part of the toluene has passed over, a viscous liquid remains, consisting of metacinnamene, held in solution by a small quantity of styrol. On pouring this liquid into alcohol, the cinnamene dissolves, while the metacinnamene is precipitated in the form of a soft colourless resin like turpentine, which may be washed with alcohol, and then dried in a stove at 150° C.

According to E. Kopp, the transformation of cinnamene into metacinnamene likewise takes place spontaneously at ordinary temperatures. This property, joined to the high refracting power of metacinnamene, suggests the possibility of using cinnamene for filling hollow glass lenses or prisms. According to Kovalevsky (Ann. Ch. Pharm. cxx. 66), metacinnamene exists also, together with cinnamene, in liquid storax.

Metacinnamene is a colourless, limpid, highly refractive substance, destitute of taste and odour. At mean temperatures it is hard, and may be cut with a knife; but it softens by heat, and may then be drawn out into long threads. It is insoluble in water and alcohol; ether dissolves it in small quantity, and at the boiling heat transforms it into a gelatinous mass, which, after drying at 100° C., forms a white spongy substance, having exactly the composition of styrol.

Metacinnamene liquefies when heated in a small retort, and yields by distillation pure cinnamene, which may be reconverted into metacinnamene by heating to 200° C. in a sealed tube.

Chlorine and *bromine* act very slowly on metacinnamene, but ultimately convert it into chloride and bromide of cinnamene respectively. Strong *sulphuric* acid carbonises it. By fusion with *hydrate of potassium* it is converted into styrol. *Nitric acid* of ordinary strength acts but slightly on metacinnamene, but fuming nitric acid dissolves it easily, with evolution of red vapours; and if the acid has been added in sufficient quantity, the solution yields with water a precipitate of nitrometacinnamene.

Compounds and Derivatives of Cinnamene.

Bromide of Cinnamene. $C^8H^8Br^2$.—Produced by the action of bromine on cinnamene. It is insoluble in water, but very soluble in alcohol and ether, whence it crystallises in needles. Solutions saturated at the boiling heat usually deposit it in the form of an oil, which remains liquid for a long time, and solidifies suddenly when agitated. It has a peculiar odour, which is not disagreeable, but excites tears. It melts at 67° C., and often remains liquid, even when cooled to 30° C., but the least agitation causes it to solidify in a crystalline mass. Its boiling point is above 200° C. It may be distilled almost wholly without alteration. Alcoholic potash converts it into bromide of potassium and a brominated organic compound.

Chloride of Cinnamene.—$C^8H^8Cl^2$. Oily liquid, produced by the action of chlorine on cinnamene. It is decomposed by distillation into hydrochloric acid and another oily compound.

Treated with alcoholic potash, it yields chlorocinnamene, C^8H^7Cl.

Trichloride of Dichlorocinnamene, $C^8H^6Cl^2.3Cl^2$, is obtained, according to Laurent, by the action of chlorine on cinnamene.

Nitrocinnamene. *Nitrostyrol.* $C^8H^7(NO^2)$.—Produced by the action of fuming nitric acid on cinnamene (p. 980). It crystallises in large prisms; has an odour of cinnamon which excites tears; produces painful blisters on the skin.

Nitrometacinnamene. Nitrometastyrol. Nitrodraconyl.—This compound, isomeric with the last, is precipitated on adding water to the product of the action of fuming nitric acid on metacinnamene. It is a white amorphous powder, insoluble in water, acids, potash, ether, and alcohol. When slightly heated, it burns with explosion. When distilled with lime, it is decomposed, with separation of carbon and evolution of ammonia, together with a small quantity of a brown oil containing phenylamine. It does not appear to be attacked by strong nitric acid, even after several hours' boiling.

CINNAMIC ACID. $C^9H^8O^2 = \left.\begin{matrix}C^9H^7O \\ H\end{matrix}\right\}O$. *Zimmtsäure. Cinnamylsäure.* (Dumas and Péligot [1834], Ann. Ch. Phys. lvii. 311.—E. Simon, Ann. Ch. Pharm. xxxi. 265.—Stenhouse, *ibid.* lv. 1; lvii. 79.—Herzog, Arch. Pharm. xvii. 72; xx. 159.—E. Kopp, Compt. chim. 1847, p. 198; 1849, p. 146; 1850, p. 140.—Cahours, Ann. Ch. Phys. [3] xxiii. 341.—Schabus, Wien Akad. Ber. 1850 [2] 206.—Chiozza, Ann. Ch. Phys. [3] xxxix. 439.—J. Löwe, J. pr. Chem. lxv. 188.—Piria, Ann. Ch. Pharm. c. 104.—Bertagnini, Cimento, iv. 46.—Gm. xiii. 268.—Gerh. iii. 388.)—This acid exists in the free state in several balsams, as in liquid storax, Tolu balsam, Peru balsam, and gum benzoin, and is often deposited in large prismatic crystals from old samples of oil of cinnamon; also from cinnamon-water.

Formation.—Cinnamic acid is produced: 1. By the action of oxidising agents on cinnamic aldehyde and on styrone.—2. By heating bitter-almond oil with chloride of acetyl in a sealed tube to 120°—130° C., but not higher, for 20—24 hours, hydrochloric acid being formed at the same time:

$$C^7H^6O + C^2H^3O.Cl = HCl + C^9H^8O^2.$$

The cinnamic acid may be extracted from the viscid residue by digestion with water containing ammonia.—3. By boiling cinnamein with potash, benzylic alcohol being formed at the same time (p. 979).—4. By fusing styracin with potash (Frémy) or boiling it with potash-ley. (Simon.)

Preparation.—*a.* From the deposit of cinnamate of lead mixed with cinnamic acid, found in the old leaden packages in which oil of cassia-cinnamon is imported. The deposit is dissolved in alcohol and filtered from the cinnamate of lead, and the alcohol is removed from the filtrate by distillation; the cinnamic acid then quickly crystallises out from the oil, and is purified by treatment with carbonate of sodium and precipitation. The residual cinnamate of lead is boiled with carbonate of sodium, filtered from the carbonate of lead, and the cinnamic acid is precipitated by dilute sulphuric acid, in silvery lustrous laminæ, which are washed, and recrystallised from alcohol (Herzog). Dumas and Péligot dissolve the crystalline deposit from oil of cinnamon in boiling water, and evaporate the filtrate to the crystallising point.

b. From Liquid Storax.—Liquid storax is distilled with water and $\frac{1}{2}$ to $\frac{7}{10}$ pts. of crystallised carbonate of sodium, whereupon styrol passes over. The residual aqueous liquid is filtered from the resin; and the filtrate is mixed at first with just so much sulphuric acid, that a very small quantity of cinnamic acid is precipitated along with dissolved resin; and the liquid filtered from this precipitate is treated with excess of sulphuric acid, which precipitates cinnamic acid of a tolerably white colour. It is dissolved in a large quantity of water, with as little carbonate of sodium as possible, and again precipitated, first with a little sulphuric acid, and then, after the filtration, with an excess of acid, by which a white precipitate is formed. This is washed with water, dried, and dissolved in alcohol, which, by spontaneous evaporation, yields quite white and very large crystals (E. Simon). Erdmann and Marchand purify the acid by distillation, pressure between paper moistened with alcohol, and repeated crystallisation. D. Howard (Chem. Soc. Qu. J. xiii. 72) finds that cinnamic acid prepared from liquid storax contains a small quantity of benzoic acid, from which, however, it is purified by crystallisation from alcohol.

c. From Balsam of Peru.—When the slimy residue which deposits in Peruvian balsam by keeping, is dissolved in warm alcohol, and the filtrate is placed in a tall and narrow cylinder with a layer of water on the top, crystals of nearly pure cinnamic acid separate in a few days from the clear brown liquid (Herberger). When Peruvian balsam is boiled with thick milk of lime, the liquid filtered, the residual magma exhausted three or four times with boiling water, and the solution again filtered, the filtrate deposits on cooling, loose, almost white masses of crystals; and these, when decomposed by hydrochloric acid, yield nearly pure cinnamic acid, which may be obtained perfectly pure, either by distillation, or by solution in ammonia, filtration, and precipitation while hot by hydrochloric acid (E. Kopp). Simon proceeds as with storax.

d. From Balsam of Tolu.—Balsam of Tolu is boiled six or seven times with solutions of carbonate of sodium, which are taken continually weaker (the last extracts only contain a little benzoic acid, produced by the action of the alkali on the resin); and the alkaline decoctions are strongly concentrated by evaporation, and precipitated hot by hydrochloric acid, whereupon most of the cinnamic acid melts into a brown resin, and but little crystallises out on cooling. The latter is pressed, the resin is pulverised, and both are dissolved in ammonia diluted with 2 pts. of water, and heated to 80° C. The greater part of the resin then remains dissolved. The liquid is filtered; the residue is boiled with water; and the whole of the very brown liquids are evaporated and decomposed, while boiling, by hydrochloric acid, whereupon most of the acid again melts, while the remainder seprates out on cooling in nearly white crystalline scales, which are pressed, and washed with a little cold water. The melted acid is also washed with a little water. The whole of the acid is heated in a porcelain dish covered with paper till the water is expelled — very little acid subliming even at 200° C.—and the fused residue is bruised and distilled. Pure cinnamic acid then passes over as a colourless, clear, strongly refracting liquid, which solidifies to a white crystalline mass like stearin. Towards the end, yellowish vapours arise, which, when collected in another receiver, solidify into a mass of acid, which is contaminated by the presence of the empyreumatic oils of the resin, but may be obtained quite pure by recrystallisation from boiling water. (E. Kopp.)

Properties.—Cinnamic acid crystallises in colourless prisms or laminæ belonging to the monoclinic system. Ordinary combination, $\infty P . [\infty P \infty] . [P \infty]$. Ratio of orthodiagonal, clinodiagonal, and principal axis = 0·3674 : 1 : 1·1694. Inclination of clinodiagonal to principal axis = 82° 58′. Cleavage perfect parallel to $[\infty P \infty]$. Specific gravity of crystals = 1·195.

Cinnamic acid dissolves sparingly in cold water, easily in boiling water, alcohol, and ether; water precipitates it from the alcoholic solution. It melts at 129° C., and boils without decomposition at 293° (Dumas and Péligot), at 300°—304° (E. Kopp), with or without decomposition, according to the manner in which it is heated. If enclosed in a sealed tube, it may be heated to 200° C. (in a paraffin-bath) for several hours without alteration. (Howard.)

Decompositions.—1. Cinnamic acid, when slowly distilled, is resolved into cinnamene and carbonic anhydride: $C^9H^8O^2 = C^8H^8 + CO^2$, a small quantity of stilbene, $C^{14}H^{12}$, being likewise produced, and passing over with the cinnamene (Howard).—2. On red-hot platinum-foil, or in the flame of a candle, it burns with a smoky flame (Bizio). On red-hot charcoal, it evaporates without flame producing a strong biting smoke.—3. Strong *sulphuric acid*, or *sulphuric anhydride*, converts it into sulpho-cinnamic acid.—4. Cinnamic acid heated with excess of *iodine*, melts to a dark brown mass; and when this mass is heated with water, and the excess of iodine expelled by evaporation, iodocinnamic acid crystallises out on cooling (Herzog).—5. *Bromine* passed over cinnamate of silver forms bromocinnamic acid (Herzog).—6. *Chlorine* passed in diffused daylight over dry cinnamic acid, forms a tough greasy substance, which, when heated with carbonate of potassium, forms chlorocinnamate of potassium, and deposits a white oil containing chlorine (Herzog). The same products are formed when chlorine is passed into warm aqueous cinnamic acid or cinnamate of sodium, and when cinnamic acid is distilled with hypochlorite of calcium (Stenhouse, E. Kopp), or with chlorate of potassium and hydrochloric acid.—7. Strong *nitric acid* converts cinnamic acid into nitrobenzoic acid, provided the mixture be kept cool; otherwise nitrous fumes are evolved, and hydride of benzoyl is first obtained, then benzoic and nitrobenzoic acids. The same products are formed on heating cinnamic acid with more dilute nitric acid. —8. Boiled with *peroxide of lead* in aqueous solution, cinnamic acid gives off the odour of bitter-almond oil, while the peroxide of lead assumes a light yellow colour, and is partially converted into benzoate of lead. This behaviour serves to distinguish cinnamic acid from benzoic acid (Stenhouse).—9. Cinnamic acid distilled with *sulphuric acid* and *acid chromate of potassium*, yields oil of bitter-almonds (Simon).—10. With *pentachloride of phosphorus* (also the trichloride, according to Béchamp), it yields chloride of cinnamyl (Cahours).—11. Fused with *hydrate of potassium*, it gives off hydrogen, and forms acetate and benzoate of potassium, a small quantity of salicylate of potassium being also produced by the action of potash on the benzoic acid previously formed (Chiozza):

$$C^9H^8O^2 + 2KHO = C^2H^3KO^2 + C^7H^5KO^2 + H^2.$$

Cinnamic acid is not decomposed by boiling with strong caustic potash (Simon).—12. In the dry distillation of the alkaline cinnamates or of cinnamic acid with *caustic baryta* or *lime*, a carbonate is formed, together with cinnamene and benzene.—13. Cinnamate of calcium, distilled with *formate of calcium*, yields cinnamic aldehyde (Piria. The reactions 6, 7, and 8, serve to distinguish cinnamic acid from benzoic acid.

CINNAMATES.—Cinnamic acid is monobasic, the formula of its salts being $C^9H^7MO^2$. They are crystallisable, and bear considerable resemblance to the benzoates. The cinnamates of the alkali-metals are easily soluble in water; those of the earth-metals and heavy metals sparingly soluble, the least soluble being the silver-salt. They dissolve more readily in water containing chlorides or nitrates.

The solutions of most cinnamates yield a precipitate of cinnamic acid when decomposed by the stronger acids. Cinnamates are decomposed by dry distillation, giving off an odour of bitter-almonds. With strong *nitric* acid, they turn yellow, and give off the odour of oil of cinnamon and bitter-almond oil. They likewise yield bitter-almond oil when distilled with *chromic* acid. With *ferric* salts, they give a yellow precipitate, and with *manganous* salts, the cinnamate being in excess, a white precipitate which soon becomes yellowish and crystalline. Benzoates give a reddish precipitate with ferric salts, and none with manganous salts. The cinnamates have been investigated chiefly by Herzog (J. pr. Chem. xxix. 51), and E. Kopp (Compt. rend. liii. 634).

Cinnamate of Aluminium.—Loose white powder, sparingly soluble in cold, easily in hot water.

Cinnamate of Ammonium, $2C^9H^7(NH^4)O^2 + aq.$—Sparingly soluble in cold water: gives off ammonia when melted, yielding a crystalline sublimate and a resinous residue. With excess of cinnamic acid, it forms an acid salt still less soluble in water. (Herzog.)

Cinnamate of Antimony and Potassium is deposited from a mixture of cinnamate of potassium and tartar-emetic, in delicate hydrated crystals, which redissolve if left for a long time in the liquid. The salt yields by calcination, a colourless residue, which effervesces with acids, and is coloured orange-red by sulphuretted hydrogen. (Herzog.)

Cinnamate of Barium, $2C^9H^7BaO^2 + aq.$—Precipitate, soluble in boiling water, crystallising on cooling. Gives off its water at 110° C. (Herzog). According to E. Kopp, the salt forms broad, irregular, transparent, nacreous laminæ containing $C^9H^7BaO^2 + aq.$ becomes anhydrous at 140° C. and when distilled with excess of barytic hydrate, yields nearly pure cinnamene.

Cinnamate of Calcium, $C^9H^7BaO^2 + aq.$—Very little soluble in cold water, easily in boiling water, whence it separates in light crystalline masses (Herzog).—$2C^9H^7CaO^2 + 3aq.$ White shining needles composed of thin nacreous laminæ, having the form of nearly rectangular parallelograms. It gives off one-third of its water when exposed to the air at ordinary temperatures, and the rest at 150° C. (E. Kopp.)

Cinnamate of Cobalt.—Rose-coloured precipitate, soluble in alcohol. (Herzog.)

Cinnamate of Copper, $C^9H^7CuO^2.xCuHO$.—The greenish-blue precipitate obtained by double decomposition, is a highly hydrated basic salt. When heated, it loses its blue colour and decomposes, giving off cinammic acid and cinnamene, and leaving metallic copper mixed with charcoal.

Cinnamates of Iron.—Both the *ferric* and *ferrous* salts are yellow precipitates, sparingly soluble in water. (Herzog.)

Cinnamate of Lead, $C^9H^7PbO^2$.—Granular crystalline powder, anhydrous and insoluble in water (Herzog). Sometimes obtained in laminæ, flattened or elongated into needles, and in small hard rounded grains (E. Kopp). Alcohol extracts a portion of the cinammic acid, leaving a basic salt.

Cinnamate of Magnesium, $2C^9H^7MgO^2 + 3aq.$, crystallised in the cold, forms small white needles, which quickly become opaque on being exposed to the air. From a boiling solution it separates in tufts of shining needles, formed by the superposition of elongated laminæ, very thin, and of nacreous aspect. It melts at 200° C. and becomes anhydrous.

Manganous Cinnamate, $C^9H^7MnO^2 + aq.$—Yellowish-white crystalline precipitate, which dissolves in boiling water acidulated with acetic acid, and separates therefrom in shining yellowish laminæ, superposed on one another. (E. Kopp.)

Mercurous Cinnamate.—White curdy precipitate.

Cinnamate of Nickel.—Green precipitate soluble in alcohol.

Cinnamate of Potassium, $2C^9H^7KO^2 + aq.$—Crystals belonging to the monoclinic system, giving off their water at 120°C, and decrepitating when strongly and suddenly heated. It is very soluble in water, but less so than the benzoate; moderately soluble in alcohol (Herzog). From a rather strong boiling solution containing excess of caustic potash, it crystallises readily in nacreous needles, which are anhydrous. (E. Kopp.)

When cinnamic acid is dissolved in a hot solution of cinnamate of potassium, a sparingly soluble *acid salt* is deposited on cooling. (Herzog.)

Cinnamate of Silver, $C^9H^7AgO^2$.—White curdy precipitate, becoming crystalline after a while; not much altered by light. It is insoluble in boiling water, but dissolves slightly in the liquid from which it has been precipitated (Herzog). White precipitate, or silky nacreous needles composed of small elongated laminæ, often bifurcated. (E. Kopp.)

Cinnamate of Sodium, $2C^9H^7NaO^2 + aq.$—Crystals with dull surface, which give off their water at 110° C. (Herzog). The anhydrous salt, $C^9H^7NaO^2 + 2aq.$, crystallises in crusts surmounted with tufts of small needles, or in compact nodules. From a solution in weak caustic soda, it crystallises in beautiful needles containing ½ at. water of crystallisation. In strong caustic soda, it dissolves but sparingly at common temperatures, separating in hard, yellowish, radiated, anhydrous spheres. (E. Kopp.)

Cinnamate of Strontium, $C^9H^7SrO^2 + 2aq.$, when recently crystallised, forms white, nacreous, nearly opaque needles, composed of very small prisms. It is much more soluble in hot than in cold water; gives off 1 at. water when exposed to dry air, and the rest at 140° C. (E. Kopp.)

Cinnamate of Tin.—The *stannic* salt is a white precipitate. (Herzog.)

Cinnamate of Uranyl.—Yellow precipitate, sparingly soluble in boiling water. (Herzog.)

Cinnamate of Zinc.—Cinnamic acid dissolves zinc at the boiling heat, with evolution of hydrogen. The salt is moderately soluble, and crystallises by evaporation (Herzog),—$C^9H^7ZnO^2 + aq.$ White precipitate, which dissolves in boiling water, and crystallises therefrom in shining, transparent, prismatic needles, sometimes grouped like mushrooms. (E. Kopp.)

CINNAMIC ETHERS. *Cinnamate of Ethyl*, $C^{11}H^{12}O^2 = C^9H^7(C^2H^5)O^2$. (Herzog, Arch. Pharm. [2] xvii. 72.—Marchand, Ann. Ch. Pharm. xxxii. 270.—E. Kopp. J. pr. Pharm. [3] xi. 72.—Plantamour, Ann. Ch. Pharm. xxx. 345).—This compound is easily obtained by distilling a mixture of 4 pts. absolute alcohol, 2 pts. cinnamic acid, and 1 pt. sulphuric acid, cohobating the product several times, agitating with water the oil which remains in the retort, and rectifying over massicot. It is a limpid liquid, of specific gravity 1·3, boiling at 262° C. (Herzog); at 266°, when the correction is made for the column of mercury projecting above the retort (H. Kopp). Vapour-density = 6·537 at 291° C. (by calculation for 2 vol. = 6·101).

Cinnamate of ethyl is nearly insoluble in water, but dissolves readily in alcohol and in ether. It is scarcely attacked by fuming nitric acid. Alkaline hydrates easily convert it into alcohol and a cinnamate of the alkali-metal.

Cinnamate of Methyl, $C^{10}H^{10}O^2 = C^9H^7(CH^3)O^2$. (E. Kopp, Compt. rend. xxi. 1376).—Obtained by saturating a mixture of cinnamic acid and wood-spirit with hydrochloric acid gas at a gentle heat, precipitating the product with water, then drying and rectifying. It is a colourless, oily liquid, having an agreeable aromatic odour. Specific gravity 1·106. Boiling point 241° C.

Cinnamate of Benzyl, or *Cinnamein* (p. 982).

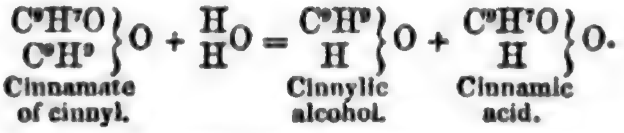
Cinnamate of Cinnyl, $C^{18}H^{16}O^2 = C^9H^7O(C^9H^9)O$. *Cinnamyl-styrone, Styracin.* (Bonastre, J. Pharm. June, 1831, p. 338.—E. Simon, Ann. Ch. Pharm. xxxi. 365.—E. Kopp, Compt. chim. 1850, p. 140.—Toel, Ann. Ch. Pharm. lxx. 1.—Strecker, *ibid.* lxx. 40; lxxiv. 112.—Plantamour, *ibid.* xxvii. 239; xxx. 341.—Gössmann, *ibid.* xcix. 376.—Scharling, *ibid.* xcvii. 90, 174.—Gm. xiii. 286.—Gerh. iii. 403.)—This compound, which bears to cinnylic alcohol or styrone (p. 992) the same relation that acetate of ethyl bears to common alcohol, is contained in liquid storax (p. 497), together with cinnamic acid, styrol, and several resins; also in balsam of Peru.

Preparation from Storax.—1. The balsam is distilled with water to expel the styrol, and then boiled with aqueous carbonate of sodium, which extracts the free cinnamic acid. The residue thus obtained is a resinous spongy mass, which contains oily styracin in its pores, and when kneaded with the fingers becomes more and more compact, while the oily styracin runs out.—2. Toel dries the resinous cake which remains after boiling the liquid storax with carbonate of sodium, after it has been freed from the solution of cinnamate of sodium; macerates it repeatedly with cold alcohol, which extracts the colouring resin, and leaves most of the styracin but little coloured; and obtains the styracin quite pure by repeated crystallisation from ether-alcohol.—3. Wolff allows the resinous cake to stand for some time in cold alcohol, when it soon becomes crystalline; frees the crystals from resin by dissolving them in boiling alcohol, and precipitating the resin with acetate of lead; and frequently recrystallises, first from ether-alcohol, then from ether.—4. After distilling liquid storax with water, and repeatedly boiling the residue with carbonate of sodium, the undissolved portion is slowly allowed to cool to 30°—40°: the mass then becomes tough and spongy, and a yellow oil collects in its pores. This oil made to run out by kneading and pressing, and then filtered, solidifies after some time into a crystalline mass, which is purified by recrystallisation from alcohol. The residual mass still contains much styracin, and is therefore worked up for styrone (E. Kopp).—5. The residue left after distilling liquid storax with water, separates when repeatedly boiled with carbonate of sodium, into a solid, dark resin, and liquid styracin. The latter is poured off, transferred to a flask, which is placed in an oil-bath at the temperature of 180° C., and distilled by passing steam heated to 180° through it; it then passes over as a white milky oil, which, when freed from water, solidifies on standing in open vessels, to a faintly coloured crystalline mass, which may be recrystallised from alcohol (Scharling).—8. Liquid storax is macerated or digested at a temperature not exceeding 30° C. with 5 to 6 pts. of dilute soda-ley, till the residue becomes colourless; this residue is collected, washed, dried and dissolved in alcohol containing ether; and from the solution, which, if not colourless, is to be rendered so by treatment with animal charcoal, pure styracin crystallises out. (Gössmann.)

Properties.—Cinnamate of cinnyl, or styracin, crystallises in tufts of beautiful prisms, destitute of taste and odour, insoluble in water, sparingly soluble in cold alcohol, very soluble in ether. It melts at 44° C. (Toel, Scharling), at 38° (E. Kopp), and remains liquid and viscous for a long time after cooling. It distils without decomposition in steam heated to 180° C. (Scharling.)

In treating storax as above described, styracin is sometimes obtained in a liquid, uncrystallisable state, especially if it has been left too long in contact with acids to free it from the last traces of soda.

Decompositions.—Styracin in contact with caustic alkalis solidifies to a mass of agglomerated granules. When distilled with potash, especially with strong alcoholic potash, it is decomposed like other compound ethers, yielding cinnylic alcohol (styrone) and cinnamate of potassium:



$$\underset{\substack{\text{Cinnamate}\\ \text{of cinnyl.}}}{\left.\begin{matrix}C^9H^7O\\ C^9H^9\end{matrix}\right\}O} + \begin{matrix}H\\ H\end{matrix}O = \underset{\substack{\text{Cinnylic}\\ \text{alcohol.}}}{\left.\begin{matrix}C^9H^9\\ H\end{matrix}\right\}O} + \underset{\substack{\text{Cinnamic}\\ \text{acid.}}}{\left.\begin{matrix}C^9H^7O\\ H\end{matrix}\right\}O}.$$

Heated with *nitric acid* it yields hydride of benzoyl, hydrocyanic acid, benzoic acid, and nitrobenzoic acid. With *chromic acid*, it yields hydride of benzoyl, benzoic acid, and a resin. With a mixture of *sulphuric acid and peroxide of manganese*, it yields hydride of benzoyl. With *strong sulphuric acid*, it yields cinnamic acid and a brown substance, soluble in water, insoluble in saline solutions.

Substitution-derivatives of Cinnamic Acid.

Bromocinnamic Acid. $C^9H^7BrO^2$.—This acid is obtained by passing bromine vapour in excess over cinnamate of silver, treating the decomposed salt with ether, and evaporating the filtered solution. A thick oil then remains, which dissolves partially in potash, and the alkaline solution decomposed by hydrochloric acid deposits crystals of bromocinnamic acid. The portion of the oil insoluble in potash is probably a bromide of carbon.

Bromocinnamic acid decomposes partially when dissolved in water and evaporated. It forms easily soluble salts with all bases, and does not precipitate nitrate of silver. (Herzog.)

Chlorocinnamic Acid. $C^9H^7ClO^2$. (E. Kopp. J. Pharm. [3] xvi. 426.—Toel, Ann. Ch. Pharm. lxx. 7.)—Obtained: 1. By passing chlorine into a cold solution of cinnamic acid in concentrated carbonate of sodium (Kopp).—2. By the action of alcoholic potash on an alcoholic solution of chlorostyracin, a chlorinated oil and chloride of potassium being formed at the same time. The mixture soon solidifies to a pulp, which is washed with alcohol, pressed, dissolved in a small quantity of boiling alcohol, and mixed with excess of hydrochloric acid. Chlorocinnamic acid then crystallises out on cooling, and may be purified by recrystallisation.

The acid crystallises in long shining odourless needles, melting at 132° C., and subliming at a higher temperature. Its vapour excites coughing. It is sparingly soluble in cold water, melts in boiling water, dissolves easily in alcohol and ether.

Chlorocinnamate of Ammonium, $2C^9H^6Cl(NH^4)O^2 + aq.$, forms curved arborescent needles. The *potassium-salt* forms lustrous pearly flakes. The *barium-salt*, $2C^9H^6ClBaO^2 + aq.$, is precipitated as a white powder, soluble in boiling water, and crystallising therefrom in shining laminæ. The *calcium-salt* is sparingly soluble, and resembles the barium-salt. The *silver-salt*, $C^9H^6ClAgO^2$, is obtained by precipitation from hot solutions, in slender needles which blacken on exposure to light.

Chlorocinnamate of Cinnyl or *Chlorostyracin*. $C^{18}H^{12}Cl^4O^2$.—Chlorine converts styracin into a viscid substance, having an acrid taste and an odour like that of copaiba balsam. It is insoluble in water, soluble in boiling alcohol and ether, whence it separates in the amorphous state. It is decomposed by potash, yielding a chlorinated oil, chlorocinnamate of potassium, and chloride of potassium. Distilled in a current of chlorine, it forms a volatile chlorinated liquid and a crystallisable chlorinated acid, the salts of which also crystallise readily. (E. Kopp.)

Nitrocinnamic Acid. $C^9H^7(NO^2)O^2$. (Mitscherlich, Ann. Ch. Phys. [3] iv. 73.—E. Kopp, Compt. chim. 1849, p. 146; Compt. rend. liii. 634.—J. Wolff, Ann. Ch. Pharm. lxxv. 303.)—This acid is produced by the action of strong nitric acid on cinnamic acid (**Mitscherlich, Kopp**), or by heating styrone with nitric acid, to which urea is added to prevent formation of nitrous acid (**Wolff**). To prepare it, concentrated nitric acid is freed from nitrous acid by boiling, and after cooling, about one-eighth of cinnamic acid is added. The cinnamic acid dissolves in a few minutes without disengagement of gas, the liquid becomes heated to 40° C., and a mass of crystals is deposited. In order to obtain larger quantities, cinnamic acid is triturated with nitric acid and cooled, so that the temperature may not rise above 50°; the mass is washed with cold water, till all nitric acid is removed, then dissolved in boiling alcohol and filtered; and the resulting crystals are washed with cold alcohol (**Mitscherlich**). Kopp dissolves 1 pt. of powdered cinnamic acid in 3 pts. of monohydrated nitric acid freed from nitrous acid by passing a dry stream of air through it, the mixture then solidifying almost immediately, in consequence of the crystallisation of the nitrocinnamic acid; washes the magma with water; then dries, and sets it aside for twenty-four hours with 4 pts. of cold alcohol, which removes any benzoic acid that may be present.

The acid forms very small white crystals, with a faint yellowish tint. It melts at about 270° C., and solidifies to a mass of crystals on cooling; boils a little above 270°, with decomposition. It is nearly insoluble in cold water, and dissolves but sparingly in boiling water; 1 pt. of it dissolves in 327 pts. of absolute alcohol at 20° C. Boiling hydrochloric acid dissolves it without decomposition (**Mitscherlich.**) With *sulphide of ammonium* it forms carbostyril. When it is dissolved in alcoholic sulphide of ammonium, sulphur separates on gently warming the liquid, while a yellow resin and an alkaloïd remain dissolved. Nitrocinnamic acid may be boiled with excess of alkali without decomposition.

Nitrocinnamic acid is but a feeble acid; nevertheless it forms neutral salts, and decomposes alkaline carbonates. The nitrocinnamates of the alkali-metals are very soluble, the rest are insoluble or sparingly soluble; they deflagrate when quickly heated, especially the potassium- and sodium-salts.

Nitrocinnamate of Ammonium gives off its ammonia when evaporated to dryness; its solution precipitates the salts of calcium, strontium, and magnesium when they are concentrated, but not when they are dilute.

Nitrocinnamate of Barium, $2C^9H^6(NO^2)BaO^2 + 3aq.$, crystallises from a boiling solution on cooling, in stellate groups of yellowish needles. The *strontium-salt*, $2C^9H^6(NO^2)SrO^2 + 5aq.$, may be obtained in small yellowish crystals grouped in nodules; it is moderately soluble in cold water. The *calcium-salt*, $2C^9H^6(NO^2)CaO^2 + 3aq.$, forms small yellowish white agglomerated grains having a crystalline aspect. The *magnesium-salt*, $C^9H^6(NO^2)MgO^2 + 3aq.$, crystallises in yellowish white nodules, which dissolve with tolerable facility in water, especially if warm.

Nitrocinnamate of Copper.—Bluish-white precipitate, which becomes darker when air-dried. When mixed with sand and distilled, it yields benzoic acid, nitrocinnamene having the odour of oil of cinnamon, and a small quantity of nitrobenzene.

Mercuric Nitrocinnamate, $C^9H^6(NO^2)HgO^2$, is thrown down from boiling solutions of mercuric chloride and an alkaline nitrocinnamate, as a brownish anhydrous precipitate. The mother-liquors deposit on cooling a crystalline mass of very light bulky arborescent tufts, consisting of the double salt, $2(HgCl.2C^9H^6(NO^2)HgO^2) + 3aq.$

Nitrocinnamate of Potassium. $C^9H^6(NO^2)KO^2$.—Very soluble; crystallises in mamellated groups by spontaneous evaporation. From solution in boiling alkaline ley, it crystallises in prismatic needles. The *sodium-salt* resembles the potassium-salt.

Nitrocinnamate of Silver. $C^9H^6(NO^2)AgO^2$.—Yellowish white insoluble precipitate, which, when cautiously heated, decomposes with projection of the silver.

NITROCINNAMIC ETHERS.—The *ethyl-compound*, $C^{11}H^{11}NO^4 = C^9H^6(NO^2)(C^2H^5)O^2$, is formed by heating nitrocinnamic acid with alcohol and sulphuric acid (**Mitscherlich**, J. pr. Chem. xxii. 194), or by the action of strong nitric acid on cinnamate of ethyl (E. **Kopp**, Compt. rend. xxiv. 615). It crystallises in prisms, which melt at 136° C.; boils with decomposition at 300°. Potash at the boiling heat converts it into alcohol and nitrocinnamate of potassium.

Nitrocinnamate of Methyl. $C^{10}H^9NO^4 = C^9H^6(NO^2)(CH^3)O^2$. (E. **Kopp**, Compt. rend. liii. 636.)—Obtained by heating nitrocinnamic acid with methylic alcohol, mixed with a small quantity of sulphuric acid or saturated with hydrochloric acid gas. The mixture thickens at first, then liquefies again, and finally a brown liquid is obtained, from which the ether separates as a crystalline mass, which may be purified by pressure and recrystallisation from alcohol. It forms white, delicate, rather elongated needles, sparingly soluble in cold alcohol and ether, and having but little odour; melts at 161° C. to a colourless liquid, which solidifies in a crystalline mass on cooling. At about 200° C. it begins to sublime in iridescent crystalline plates, and at 200° it boils. It dissolves in alcoholic sulphydrate of ammonium, forming a red liquid, which afterwards turns brown, and when heated yields an abundant crystallisation of sulphur.

CINNAMIC ALCOHOL. See Cinnylic Alcohol.

CINNAMIC ALDEHYDE. See Cinnamyl, Hydride of.

CINNAMIC ANHYDRIDE. $C^{18}H^{14}O^3 = (C^9H^7O)^2.O$. *Cinnamate of Cinnamyl. Cinnamic Cinnamate, Anhydrous Cinnamic Acid.* (Gerhardt, Ann. Ch. Phys. [3] xxxvii. 285.)—Produced by the action of oxychloride of phosphorus on well dried cinnamate of sodium, the best proportions being 1 pt. of the former to 6 pts. of the latter. The product is washed with water and carbonate of sodium, then dried and dissolved in boiling alcohol. It may also be obtained by the action of chloride of cinnamyl on neutral oxalate of potassium. It crystallises from the alcoholic solution as a white crystalline substance, composed of microscopic needles. It is insoluble in cold alcohol, and dissolves but slightly even in boiling water, becoming acid at the same time. It melts at 127° C.

Aceto-cinnamic Anhydride. $C^2H^3O.C^9H^7O.O$. See Acetic Anhydride (p. 21).

Benzo-cinnamic Anhydride. $C^7H^5O.C^9H^7O.O$. See Benzoic Anhydride (p. 558).

Nitrocinnamic Anhydride. $C^{18}H^{12}N^2O^7 = [C^9H^6(NO^2)O]^2.O$. (Chiozza, Ann. Ch. Phys. [2] xxxix. 231.—Gerh. iii. 388.)—Produced by the action of oxychloride of phosphorus on nitrocinnamate of potassium. It melts in boiling water more easily than nitrocinnamic acid, forming a yellow kneadable resin. It easily takes up water, and is converted into nitrocinnamic acid. With ammonia, it easily forms nitrocinnamide and nitrocinnamate of ammonium. With alcohol, it forms nitrocinnamate of ethyl. It is sparingly soluble in ether.

CINNAMIC ETHERS. See page 986.

CINNAMIDE. $C^9H^9NO = N.H^2.C^9H^7O$.—Chloride of cinnamyl treated with dry ammonia, yields sal-ammoniac, together with a white substance which dissolves in boiling alcohol, and separates in delicate needles in cooling. (Cahours.)

Nitrocinnamide. $C^9H^8N^2O^3 = N.H^2.C^9H^6(NO^2)O$. (Cahours, Ann. Ch. Phys. [3] xxvii. 452.)—Prepared: 1. By the action of aqueous ammonia on the product obtained by treating nitrocinnamate of potassium with oxychloride of phosphorus. After an hour's digestion at a gentle heat, the reaction is complete, and the nitrocinnamic anhydride is completely transformed into nitrocinnamide and nitrocinnamate of ammonium, which remains in solution. The nitrocinnamide is collected on a filter and purified by crystallisation from boiling water.—2. By the action of alcoholic ammonia on nitrocinnamate of ethyl; this process, however, takes a long time, and requires a large quantity of alcohol.

Nitrocinnamide separates from solution in boiling water in shortened, lustrous needles, sometimes in grains and laminæ having the appearance of flies' wings. It melts and turns brown between 155° and 160° C., and decomposes completely at 260°. It dissolves sparingly in cold alcohol, moderately in ether, and separates from solution in boiling alcohol in small, very regular, hemispherical concretions, smooth in the upper, and nodular in the lower part. It dissolves in caustic potash, producing a red solution, without evolution of ammonia.

Phenyl-Cinnamide. *Cinnanilide.* $N.H.C^6H^5.C^9H^7O$. (Cahours, Ann. Ch. Phys. [3] xxiii. 344.)—Produced by the action of phenylamine on chloride of cinnamyl. It dissolves easily in hot alcohol, and separates in slender needles on cooling. It melts at a gentle heat, and distils completely at a higher temperature. Potash-solution scarcely attacks it, even with aid of heat; but when fused with hydrate of potassium, it gives off phenylamine.

Nitranisyl-Cinnamide. *Cinnitranisidine.* $C^{16}H^{14}N^2O^4 = N.H.C^7H^6(NO^2)O.C^9H^7O$.—Produced by the action of chloride of cinnamyl on nitranisidine (p. 304). Yellowish needles, sparingly soluble in cold, more soluble in boiling alcohol. (Cahours.)

CINNANILIDE. Syn. with Phenyl-Cinnamide (*vid. sup.*)

CINNHYDRAMIDE. $C^{27}H^{24}N^2 = N^2(\overset{\prime\prime}{C^9H^8})^3$.—A compound produced by the action of ammonia on hydride of cinnamyl. It is analogous to hydrobenzamide, $C^{21}H^{18}N^2$, and is therefore more properly called hydrocinnamide (*q. v.*)

CINNAMON, OIL OF, and **OIL OF CASSIA.** These oils, which are nearly identical in composition, are obtained from the bark of different trees of the genus *Cinnamonum*, order *Lauraceæ*, viz. oil of cinnamon from Ceylon cinnamon, *Cinnamomum Zeylanicum;* and oil of cassia, from the bark of Chinese cinnamon, *Cinnamomum aromaticum*, or from *cassia buds*, the undeveloped flowers of *Cinnamomum Lauresii* (Nees). The oils are prepared by softening the bruised bark or flowers with salt water, distilling quickly, and drying with chloride of calcium. Oil of cinnamon has a more agreeable odour than oil of cassia, and is therefore more esteemed.

Both the oils consist mainly of cinnamic aldehyde, which may be separated by means of an acid sulphite of alkali-metal (p. 991); also a hydrocarbon, not yet examined, in variable, but always very small quantity, together with cinnamic acid, and resins.

Old samples often deposit crystals of cinnamic acid. The density of the oils varies from 1·025 to 1·05; their boiling point from 220° to 225° C.

Resins from Cinnamon-oil.—Old samples of the oil are more or less coloured and charged with resinous matters, which remain, after the oil has been distilled with salt water, the residue treated with cold water, to extract the salt, and afterwards with boiling water, to extract cinnamic acid. According to Mulder (Ann. Ch. Pharm. xxxiv. 149), there are two resins formed in the oil by atmospheric oxidation; one, α, soluble in cold alcohol, melting at 60° C., and containing 78·33 per cent. carbon, 6·49 hydrogen, and 15·18 oxygen; the other, β, sparingly soluble only in hot alcohol, melting at 145°, and containing 83·45 per cent. C, 6·06 H, and 10·49 O.

Mulder likewise describes several other resins, some soluble, others insoluble in alcohol, produced by treating oil of cinnamon with sulphuric acid, hydrochloric acid, and ammonia: they have all nearly the same composition as the β-resin, produced by atmospheric oxidation. (Gm. xiii. 264.)

CINNAMON-STONE. A variety of garnet (*q. v.*)

CINNAMYL. C^9H^7O.—The monatomic radicle of cinnamic acid and its derivatives. The following is a list of its compounds, and of those of the derived radicles, chlorocinnamyl, &c.

Type HH:

Chloride of Cinnamyl	$C^9H^7O.Cl$
Cyanide of Cinnamyl	$C^9H^7O.Cy$
Hydride of Cinnamyl: *Cinnamic Aldehyde*	$C^9H^7O.H$
Hydride of Tetrachlorocinnamyl: *Chlorocinnose*	$C^9H^3Cl^4O.H$

Type HHO:

Hydrate of Cinnamyl: *Cinnamic Acid*	$C^9H^7O.H.O$
Hydrate of Bromocinnamyl: *Bromocinnamic Acid*	$C^9H^6BrO.H.O$
Hydrate of Chlorocinnamyl: *Chlorocinnamic Acid*	$C^9H^6ClO.H.O$
Hydrate of Nitrocinnamyl: *Nitrocinnamic Acid*	$C^9H^6(NO^2)^2O.H.O$
Oxide of Cinnamyl: *Cinnamic Anhydride*	$(C^9H^7O)^2O$
Oxide of Cinnamyl and Acetyl: *Aceto-cinnamic Anhydride*	$C^9H^7O.C^2H^3O.O$
Oxide of Cinnamyl and Benzol: *Benzo-cinnamic Anhydride*	$C^9H^7O.C^7H^5O.O$
Oxide of Nitrocinnamyl: *Nitrocinnamic Anhydride*	$[C^9H^6(NO^2)O]^2O$

Type NH^3:

Cinnamide	$N.H^2.C^9H^7O$
Phenyl-cinnamide: *Cinnanilide*	$N.H.C^6H^5.C^9H^7O$
Nitranisyl-cinnamide: *Cinnitranisidine*	$N.H.C^7H^6(NO^2)O.C^9H^7O$

The compounds of cinnamyl are intimately related to those of benzoyl, C^7H^5O, and are easily converted by oxidising reagents into hydride of benzoyl and benzoic acid. Cinnamic acid heated with excess of hydrate of potassium, is resolved, with evolution of hydrogen, into acetic and benzoic acids (p. 984).

CINNAMYL, CHLORIDE OF. $C^9H^7O.Cl$. (Cahours, Ann. Ch. Phys. [3] xxiii. 341.—Béchamp, Compt. rend. xlii. 224.)—This compound is produced by the action of trichloride or pentachloride of phosphorus on cinnamic acid. When the pentachloride is used, the product is distilled, the portions which pass over between 250° and 265° C. being collected apart and rectified (Cahours). With the trichloride, the mixture must be heated to between 60° and 120° C., as long as hydrochloric acid continues to escape. It then melts and forms two layers, the upper of which, consisting of chloride of cinnamyl, is decanted and distilled. (Béchamp.)

Chloride of cinnamyl is a heavy oil, of specific gravity 1·207, boiling at 262° C. In a moist atmosphere it decomposes quickly, yielding hydrochloric acid and fine crystals of cinnamic acid. In contact with alcohol, it becomes strongly heated, and if water be then poured upon the mixture, cinnamate of ethyl separates as a heavy oil. With ammonia and phenylamine, it yields cinnamide and phenyl cinnamide respectively. Heated with cinnamate of sodium, it yields cinnamic anhydride.

CINNAMYL, CYANIDE OF. $C^{10}H^7NO = C^9H^7O.Cy$. (Cahours, *loc. cit.*)—Produced by distilling chloride of cinnamyl with cyanide of potassium or cyanide of mercury. A liquid then passes over, which rapidly turns brown when exposed to the air, yielding hydrocyanic and cinnamic acids. It still contains chlorine, but consists for the most part of cyanide of cinnamyl.

CINNAMYL, HYDRIDE OF. $C^9H^8O = C^9H^7O.H$. *Cinnamic Aldehyde.* (Dumas and Péligot, Ann. Ch. Phys. lvii. 305.—Mulder, Ann. Ch. Pharm. xxxiv.

147.—**Bertagnini**, *ibid.* lxxxv. 272.—**Gm.** xiii. 258.—**Gerh.** iii. 373.)—This compound forms the essential part of oil of cinnamon or oil of cassia, and may be separated therefrom by the action either of nitric acid or of the acid sulphites of the alkali-metals.

a. When commercial oil of cinnamon is shaken up with strong nitric acid, large crystals are formed, after two or three hours, consisting of a compound of nitric acid with cinnamic aldehyde, which, when collected on a filter, so as to allow the still liquid portion to drain off, and then decomposed by water, yields pure cinnamic aldehyde. (**Dumas** and **Péligot.**)

b. Oil of cinnamon is agitated with three or four times its volume of a solution of acid sulphite of potassium of 28°—30° Bm; and the crystalline mass, which forms in a few minutes, is separated from the mother-liquor, left to dry on a filter, then pulverised, washed with cold alcohol, again dried, and dissolved at a gentle heat in dilute sulphuric acid. A large quantity of sulphurous acid is then given off, and the cinnamic aldehyde rises to the surface as an oil, which may be purified by washing and drying.

Cinnamic aldehyde is a colourless oil rather heavier than water. It may be distilled without decomposition, either in vacuo, or with water which has been freed from air by boiling. When exposed to the *air*, it quickly becomes yellow and resinous, and acquires an acid reaction. It rapidly absorbs *oxygen* gas, especially if moist, and is thereby converted into cinnamic acid. Heated with *nitric acid*, it forms benzoic acid and hydride of benzoyl. *Chromic* acid converts it into benzoic and acetic acids (**Persoz**). Boiled with solution of *hypochlorite of calcium*, it yields benzoate of calcium. Strong *sulphuric acid* converts it into a resinous mass.

Cinnamic aldehyde gradually heated in a stream of *chlorine*, forms at first a liquid compound, which solidifies when treated with a strong solution of potash. When distilled four or five times in a stream of chlorine, it is converted into tetrachlorocinnamyl. With *pentachloride of phosphorus*, it yields hydrochloric acid and chloride of cinnamyl. Fused with *hydrate of potassium*, it forms cinnamate of potassium, with evolution of hydrogen:

$$C^9H^8O + KHO = C^9H^7KO^2 + H^2.$$

Ammonia-gas converts it into cinnhydramide:

$$3C^9H^8O + 2NH^3 = C^{27}H^{24}N^2 + 3H^2O.$$

Compounds of Cinnamic Aldehyde.

a. *With Hydrochloric Acid.*—Oil of cinnamon absorbs a large quantity of hydrochloric acid gas, acquiring a green colour and becoming thicker. 100 pts. of the oil take up 26·9 pts. of hydrochloric acid.

b. *With Iodine and Iodide of Potassium.*—When cinnamon-water is placed in contact with iodine and iodide of potassium and cooled to 0° C., a crystallisable compound, $C^9H^8O.I^8.KI$, is formed. It crystallises from alcohol and ether, but water decomposes it, setting free the cinnamic aldehyde. An excess of iodide of potassium prevents the decomposition. (**Apjohn**, Ann. Ch. Pharm. xxviii. 314.)

c. *With Nitric Acid.* $C^9H^8O.HNO^3$.—Produced when strong nitric acid is left in contact with cinnamic aldehyde. It forms oblique, rhomboïdal prisms, often two or three inches long. After being drained, they may be preserved for some hours, but the least rise of temperature or atmospheric humidity quickly decomposes them. When treated with water, they yield pure cinnamic aldehyde.

Nitrate of cinnamic aldehyde kept in an imperfectly closed vessel, yields after a few days a red liquid, which has the characteristic odour of bitter-almond oil, is converted by ammonia-gas into nitrate of ammonium and a red resin; and is dissolved by strong sulphuric acid, the solution yielding with water a precipitate of cinnamic acid.

d. *With Acid Sulphites of Alkali-metals.*—Cinnamic aldehyde dissolves easily in aqueous acid sulphite of ammonium, forming an oily liquid, which afterwards solidifies to a crystalline pulp. Oil of cassia shaken up with a strong solution of acid sulphite of ammonium soon solidifies to a yellow crystalline mass, which may be purified from the hydrocarbon and other substances which the oil contains, in addition to cinnamic aldehyde, by washing with alcohol of 80 or 90 per cent. (**Gössmann**). The compound is very unstable, quickly turning brown, even when kept in closed vessels.

The *potassium-salt* is obtained by agitating oil of Ceylon or Chinese cinnamon with three or four times its volume of a solution of acid sulphite of potassium of 28° to 30° Bm.; after washing with alcohol and recrystallisation from boiling alcohol, it forms beautiful silvery plates nearly inodorous and permanent in the air. It is soluble in cold water, but the solution is decomposed by heat, giving off sulphurous acid and yielding colourless drops of cinnamic aldehyde. Heated in a test-tube, it gives off water, sulphurous acid, and cinnamic aldehyde, which, by contact with the air, is converted into cinnamic acid. Bromine and iodine dissolve in the aqueous solution without colouring it, but converting the sulphurous acid into sulphuric acid, and setting free the cinnamic aldehyde. Bromine in excess produces a solid, slightly aromatic substance fusible in hot water.

Sodium-salt.—Oil of cinnamon mixed with solution of acid sulphite of sodium of 37° Bm. forms a crystalline fibrous substance, which, if left to itself, soon becomes completely liquid; at the same time there is formed an oil which is not solidified, either by acid sulphites of alkali-metal or by nitric acid, the sulphite of cinnamyl-sodium apparently remaining dissolved. The liquid, if left to evaporate, yields crystals of sulphate of sodium, together with opaque crystalline nodules, which dissolve in boiling alcohol, forming a solution which on cooling deposits long thin needles arranged in spiral groups. (Bertagnini.)

Hydride of Tetrachlorocinnamyl. *Chlorocinnose.* $C^9H^3Cl^4O.H$. (Dumas and Péligot, Ann. Ch. Phys lvii. 316.)—By repeatedly distilling hydrate of cinnamyl in chlorine gas, this compound is obtained in long white very volatile needles. It melts at a gentle heat and sublimes without decomposition. It is soluble in alcohol. It is not decomposed by strong sulphuric acid, even at the boiling heat, and may be volatilised without alteration in a current of dry ammonia.

The formation of this substance is preceded by that of several liquid compounds, one of which, perhaps *hydride of monochlorocinnamyl*, solidifies in contact with potash-ley.

CINNYL. C^9H^9.—The radicle of the compound usually called *cinnamic* alcohol or *styrone.* Cinnyl bears to cinnamyl, C^9H^7O, the radicle of cinnamic acid, the same relation that ethyl, C^2H^5, bears to acetyl, C^2H^3O.

CINNYLIC ALCOHOL. $C^9H^{10}O = C^9H^9.H.O$. *Hydrate of Cinnyl, Cinnamic Alcohol, Styrone, Styracone, Styrax-Alcohol, Styrylic Alcohol, Peruvin.* (E. Simon, Ann. Ch. Pharm. xxxi. 274.—Toel, *ibid.* lxx. 3.—Strecker, *ibid.* lxx. 10.—J. Wolff, *ibid.* lxxxv. 299.—E. Kopp, Compt. chim. 1850, p. 113.—Scharling, Ann. Ch. Pharm. cxv. 90, 183.—Gm. xiii. 256.—Gerh. iii. 402.)—This compound is obtained by cautiously distilling styracin with a strong solution of caustic potash or soda. A milky liquid then passes over, from which, when saturated with common salt, a creamy substance separates, gradually collecting on the surface in an oily layer and solidifying (Toel). Wolff dissolves styracin in boiling alcoholic potash; mixes water with the liquid; filters from cinnamate of potassium; and separates the precipitated cinnamic alcohol from undecomposed styracin by distillation.

Cinnylic alcohol forms beautiful soft silky needles, having a sweet taste and an agreeable odour of hyacinths. It melts at 33° C., and volatilises without alteration at a higher temperature. It is moderately soluble in water, very soluble in alcohol, in ether, in styrol, and in oils, both fixed and volatile. When the aqueous solution saturated at the boiling heat is left to cool, it becomes milky, and does not clarify for several hours, when it becomes filled with needle-shaped crystals.

CIPOLINO. A white marble with shadings or zones of green talc, found in Italy.

CISSAMPELINE. Syn. with Pelosine (*q. v.*)

CITRACONAMIDES and **CITRACONANILIDES.** See Amides of Citraconic Acid (p. 993).

CITRACONIC ACID. *Pyrocitric Acid.* $C^5H^6O^4$. (Lassaigne [1822], Ann. Ch. Phys. xxi. 100.—Dumas, *ibid.* cxi. 21.—Robiquet, *ibid.* lxv. 78.—Liebig, Ann. Ch. Pharm. xxvi. 119, 152.—Crasso, *ibid.* xxxiv. 68.—Engelhardt, *ibid.* lxx. 246.—Gottlieb, *ibid.* lxxvii. 265.—Baup, Ann. Ch. Phys. [3] xxxiii. 192.—Gm. x. 417.—Gerh. ii. 120.)—This acid, or rather its anhydride, is produced by the dry distillation of citric acid, constituting in fact the chief portion of the distillate (p. 995). The anhydride rapidly attracts moisture, and when exposed to the air, is converted into a crystalline mass of citraconic acid, which is freed from excess of water by pressure between blotting-paper and exposure to a temperature of 50° C. Citraconic acid is also one of the products of the dry distillation of lactic acid.

Citraconic acid is inodorous, and has a sour and slightly bitter taste. It crystallises in four-sided prisms, dissolves in 8 pts. of water at 10° C., and is readily soluble in alcohol and in ether. It melts at 80° C.; small quantities of it kept for some time at 100° are converted into itaconic acid. By dry distillation it is resolved into citraconic anhydride and water.

When citraconic acid is heated with strong *nitric acid*, a violent reaction is set up, accompanied by disengagement of gas, and an oily body is produced, which on cooling solidifies to a crystalline mass, consisting of two crystalline nitro-compounds, eulyte and dyslyte, which dissolve in alcohol to an unequal extent; their composition is not known. By *dilute nitric acid*, citraconic acid is converted into *mesaconic acid.*

When *bromine* is gradually added to a strong solution of citraconate of potassium, carbonic acid is disengaged and a heavy yellowish oil separates, consisting of an acid and a neutral substance. The former is removed by treatment with dilute potash, which leaves the latter unaltered. When a weak acid is added to the alkaline solution, there is separated, sometimes a heavy oil and sometimes fine needles. These two bodies are identical in composition, and consist of an acid, $C^4H^6Br^2O^2$, which has been named by Cahours, its discoverer, *bromotriconic acid.* It has the composition of dibrominated butyric acid (p. 693); but Cahours did not obtain it by the action of bromine on butyric acid or butyrate of potassium. The liquid acid is slightly amber-coloured, and has a peculiar odour. When distilled, it gives off hydrobromic acid and leaves a carbonaceous residue. The liquid acid, after standing for some time, occasionally solidifies to a mass of crystals. When it is heated with concentrated potash, a peculiar odour is disengaged, and the addition of an acid no longer precipitates an oil. The acid forms a curdy precipitate with silver-solution, and its ammonium-salt crystallises.

The neutral oil formed in the preparation of the acid has the composition $C^3H^3Br^3O$, and may either be *tribromopropionic aldehyde* or *tribrominated acetone.*

By the action of *bromine* on citraconate of potassium, in presence of excess of hydrate of potassium, an oil is also separated and carbonic acid disengaged. When a weak solution of potash is added, the greater part dissolves, and a small quantity of tribromopropionic aldehyde remains; on adding dilute nitric acid to the alkaline solution, large white crystalline flakes are deposited, consisting of an acid which crystallises from alcohol and ether in long prisms. It has the composition of dibromopropionic acid, $C^3H^4Br^2O^2$, but Cahours names it bromitonic acid.

CITRACONATES.—Citraconic acid is a dibasic acid, and forms two series of salts, the *neutral salts*, $C^5H^4M^2O^4$, and the *acid salts*, $C^5H^5MO^4$; they are isomeric with the itaconates, mesaconates, and lipates. The acid salts mostly crystallise well.

The *acid barium-salt*, $C^5H^5BaO^4$, crystallises in large groups of fine silky needles.

The *neutral silver-salt*, $C^5H^4Ag^2O^4$, crystallises both anhydrous and with an atom of water. In an aqueous solution of citraconic acid, nitrate of silver produces, on addition of ammonia, a very bulky precipitate which dissolves in boiling water. On cooling, the salt is deposited in long needles. If the mother-liquor from this be slowly evaporated, hexagonal crystals are formed which have an adamantine lustre, and consist of the hydrated salt, $C^5H^4Ag^2O^4 + H^2O$.

The *acid silver-salt*, $C^5H^5AgO^4$, is obtained by dissolving the neutral salt in an acid solution of citraconic acid. On evaporation, large groups of crystals are obtained.

Citraconate of Ethyl, or *Citraconic Ether*, $C^9H^{14}O^4$, is obtained by repeatedly cohobating a mixture of alcohol, citraconic acid, and hydrochloric acid, and washing the distillate with water.

It is a colourless, bitter, somewhat aromatic liquid, of density 1·040 at 18°·5 C. It boils at 225° C. with partial decomposition. It is insoluble in water, but readily soluble in alcohol and in ether. In contact with water, it gradually acidifies and alcohol is formed. By potash it is decomposed into citraconate of potassium and alcohol. E. A.

CITRACONIC ACID, AMIDES OF:

CITRACONAMIDE, $C^5H^8N^2O^2 = N^2.H^4.(C^5H^4O^2)''$, is obtained as a yellow viscid mass, which becomes brittle and vitreous on cooling, when citraconic anhydride is heated in a stream of dry ammoniacal gas. It dissolves in water, and the solution on cooling yields citraconate of ammonium. It is derived from neutral citraconate of ammonium by the loss of 2 at. of water:

$$C^5H^4(NH^4)^2O^4 - 2H^2O = C^5H^8N^2O^2.$$

CITRACONIMIDE. $C^5H^5NO^2 = N.H.(C^5H^4O^2)''$.—Citraconic acid is mixed with excess of ammonia and evaporated to dryness, and the residue heated to 180° C. An amorphous oily yellow mass is left, which is citraconimide. It does not dissolve in cold water, and but slightly so in alcohol; it is highly hygroscopic. It is derived from acid citraconate of ammonium by the loss of 2 at. of water:

$$C^5H^5(NH^4)O^4 - 2H^2O = C^5H^5NO^2.$$

Phenylcitraconimide or *Citraconanil.* $C^{11}H^9NO^2 = N.C^6H^5.(C^5H^4O^2)''$.—When anhydrous citraconic acid is mixed with phenylamine, a brisk action ensues, and the mixture, if kept for some time in the water-bath, is totally converted into the above compound. It crystallises in colourless needles, which melt at 96° C., and sublime at a little above 100°. It is readily soluble in alcohol and in ether.

It is derived from acid citraconate of phenylamine by the loss of 2 at. of water:

$$C^5H^5(C^6H^8N)O^4 - 2H^2O = C^{11}H^9NO^2.$$

Iodophenylcitraconimide, $C^{11}H^8INO^2$, is obtained by substituting iodophenylamine in the above reaction.

Dinitrophenylcitraconimide, $C^{11}H^7(NO^2)^2NO^2$, is obtained by the action of a mixture of nitric and sulphuric acid on phenylcitraconimide.

Citraconamic Acid. $C^5H^7NO^3 = N.\overbrace{H^2.C^5H^4}^{'''}\overbrace{O^2.H}^{''}.O$.—Citraconimide appears to be partially convertible into this acid by boiling with ammonia. Its salts are uncrystallisable.

Phenylcitraconamic Acid, $C^{11}H^{11}NO^3 = N.H.\overbrace{C^6H^5.C^5H^4}^{'''}\overbrace{O^2.H}^{''}.O$, is obtained as an ammonium-salt by boiling phenylcitraconimide with dilute ammonia. On the addition of acetic acid, it is separated as a crystalline precipitate, which is washed with cold water. It is an unstable body. It is derived from acid citraconate of phenylamine by the loss of an atom of water:

$$C^5H^5(C^6H^8N)O^4 - H^2O = C^{11}H^{11}NO^3.$$

Dinitrophenylcitraconamic acid, $C^{11}H^9(NO^2)^2NO^3$, is obtained in a similar manner.
E. A.

CITRACONIC ANHYDRIDE. $C^5H^4O^3$.—This compound is produced by the dry distillation of citric acid, constituting the greater part of the crude product. On rectifying this crude distillate, two layers are formed, the upper being aqueous, and the lower an oily acid liquid which does not solidify.. This, which is citraconic anhydride, is purified by redistillation. The same substance is formed by heating itaconic acid.

Citraconic anhydride is a colourless inodorous liquid of specific gravity 1·247. It rapidly absorbs ammonia, with disengagement of heat, forming a vitreous deliquescent mass, which probably consists of citraconamic acid. E. A.

CITRACONIC CHLORIDE. *Pyrocitric Chloride, Chloride of Pyrocitryl.* $C^5H^4O^2Cl^2$.—When pentachloride of phosphorus is mixed with citraconic anhydride, a brisk action ensues, and on subsequent distillation, oxychloride of phosphorus passes over, followed by chloride of pyrocitryl when the temperature has reached 175° C. It contains, however, some citraconic anhydride, which raises the boiling point: it is freed therefrom by redistillation with pentachloride of phosphorus, the part distilling between 175°—190° being ultimately collected. It is a highly refracting fuming liquid, with a density of 1·4. With water, it forms citraconic and hydrobromic acids, and with absolute alochol, citraconic ether and hydrochloric acid. E. A.

CITRACONIC ETHER. See CITRACONATES (p. 993).

CITRAMIDES. See page 1000.

CITRACONIMIDE (p. 993).

CITRACONIODANIL. Syn. with IODOPHENYLCITRACONIMIDE (p. 993).

CITRENE. *Citronyl.* $C^{10}H^{16}$.—A liquid isomeric with oil of lemon, &c., obtained by distilling the solid di-hydrochlorate of lemon-oil over hydrate of potassium or quick lime. It is transparent and colourless, of specific gravity 0·8569, vapour-density 4·73 (by calculation for 2 vol. 4·71); boils at 165° C. It resembles oil of lemon in most of its properties, and in forming a crystallisable compound with hydrochloric acid, but differs from it in being without action on polarised light. (Gm. xiv. 303.)

CITRIC ACID. $C^6H^8O^7 = C^6H^5O^4.H^3.O^3$. (Scheele [1784], *Opuscula* ii. 181. —Berzelius, Ann. Chim. xciv. 171; Ann. Ch. Phys. lii. 424, 432; lxvii. 303; lxx. 215.—Robiquet, *ibid.* lxv. 68.—Liebig, Ann. Ch. Pharm. v. 134; xxvi. 119, 152; xliv. 57.—Marchand, J. p. Chem. xxiii. 60.—Cahours, Ann. Ch. Phys. [3] xix. 488.—Pebal, Ann. Ch. Pharm. lxxxii. 78; xcviii. 67.—Gm. xi. 436.—Gerh. ii. 85.) —The existence of a peculiar organic acid in the juice of lemons and of oranges has long been known, but the discovery of the separate identity of this acid, and its discrimination from tartaric acid, was first effected by Scheele in 1784, who gave to it the name it bears.

It is to the presence of citric acid that a great many fruits owe their acidity. This acid occurs in the free state in oranges, lemons, citrons, tamarinds, cherries, currants, gooseberries, raspberries, strawberries, whortleberries, and a great many others. In some of them it is associated with malic and tartaric acids. It is also contained in several tubers and bulbs, such as the potato and the onion. Occasionally it occurs as acid potassium or calcium salt.

Preparation.—The raw material for the production of citric acid is lemon juice. The juice is made to undergo an incipient fermentation; it is then filtered and neutralised, first with chalk and afterwards with quick lime, by which an insoluble citrate of calcium is formed: 10 pts. of this salt are carefully decomposed by a cold mixture of 9 pts. sulphuric acid and 56 of water; the gypsum is washed with cold water; and the filtrate and wash-water are boiled down in a leaden vessel over the naked fire until the liquor has the specific gravity 1·13, then concentrated over a water-bath until a saline film begins to form, when the liquid is immediately cooled to the crystallising point; if it were further concentrated, the excess of sulphuric acid would convert the residue into a black mass. The crystals formed are purified by four or five recrystallisations, and the mother-liquors are utilised for the preparation of citric acid by treatment with chalk, in the same manner as the fresh lemon juice. In the south of France, the citrate of calcium is bleached with chloride of lime, prior to its decomposition with sulphuric acid. Good lemons yield about 5½ per cent. of the crystallised acid.

The raw material generally used in this country for the preparation of citric acid on the large scale, for the use of calico-printers, is a black fluid, like thin treacle, which comes from Sicily, and is obtained by inspissating the expressed juice of the lemon after the rind has been removed for the sake of the essential oil. (*Ure's Dictionary of Arts, Manufactures and Mines*, i. 690.)

Citric acid may also be prepared from gooseberries. Tilloy (J. Pharm. xiii. 305) expresses the juice of the unripe berries; leaves it to ferment; distils off the alcohol formed; filters the residual liquid; and treats it with chalk in the same manner as in the preparation of the acid from lemon juice. 100 pounds of gooseberries give 10 pounds of spirit of specific gravity 0·928, and 1 pound of crystallised citric acid.

Properties.—Citric acid crystallises in two forms. A concentrated solution deposits by spontaneous evaporation, large, transparent, colourless prisms, having the composition $C^6H^8O^7 + H^2O$; this is the ordinary commercial acid. The crystals belong to the trimetric system, and generally have the faces $\infty P \,.\, \bar{P}\infty \,.\, \breve{P}\infty$ predominant, also with $\infty \bar{P} \infty$; the face $2\breve{P}\infty$ likewise occurs together with $\bar{P}\infty$, and sometimes without it. P also not unfrequently occurs subordinate. Ratio of brachydiagonal, macrodiagonal, and principal axis = 0·6068 : 1 : 0·4106. (*Kopp's Krystallographie*, p. 264; see also Gerh. ii. 88.) The crystals effloresce in the air between 28° and 50° C., and lose their water of crystallisation at 100°. A boiling concentrated solution of citric acid allowed to cool, deposits crystals of a different form, which, according to some chemists, contain $2C^6H^8O^7 + H^2O$; according to others, this water is only mechanically mixed.

Citric acid has a strong, but pleasant, acidity, in which respect it differs from tartaric acid, the acidity of which is accompanied by a somewhat bitter taste. This difference is still greater in the salts.

Citric acid is soluble in 0·75 pts. of cold and in 0·5 pts. of boiling *water*. It is readily soluble in *alcohol*, but insoluble in *ether*.

Citric acid and its potassium-salt are used in medicine. It is also used in the preparation of effervescent summer beverages. Its most extensive application is in dyeing and calico-printing; for certain of the finer colours, it cannot be replaced by less costly acids.

When *lime-water* is added to a solution of citric acid, a slight precipitate is formed, if the solution is concentrated and the lime-water present in great excess. But if the mixture be boiled, a considerable precipitate of citrate of calcium is formed, which redissolves as the solution cools. By this deportment, free citric acid is easily detected. It is distinguished from tartaric and racemic acids by the fact that its potassium-salt is soluble.

Decompositions.—1. Solution of citric acid, when kept for some time, becomes covered with fungi.—2. An aqueous solution mixed with chalk and exposed for some time to a temperature of 20°—30° C. in contact with a little *yeast*, yields acetic and butyric acids. According to How, when exposed in contact with *putrefying curd* and a base, it ferments and becomes converted into acetic and propionic acids.—3. When citric acid is heated in a retort, it first melts in its water of crystallisation and then boils, giving off the water, which condenses in the receiver. Afterwards at about 175° C. vapours of acetone distil over, and a copious disengagement of carbonic oxide takes place. At this time, the residue in the retort consists of aconitic acid. If the distillation be continued, carbonic acid is given off and oily striæ begin to appear in the neck of the retort, which solidify to crystals of itaconic acid. If these last crystals be repeatedly distilled, an oily mass of anhydrous citraconic acid is obtained, which no longer solidifies. These decompositions of citric acid are thus expressed:

$$\underset{\text{Dry citric acid.}}{C^6H^8O^7} \quad - \quad H^2O \quad = \quad \underset{\text{Aconitic acid.}}{C^6H^6O^6}.$$

$$\underset{\text{Aconitic acid.}}{C^6H^6O^6} \quad - \quad CO^2 \quad = \quad \underset{\text{Crystallised itaconic acid.}}{C^5H^6O^4}.$$

$$\underset{\text{Crystallised itaconic acid.}}{C^5H^6O^4} \quad - \quad H^2O \quad = \quad \underset{\text{Citraconic anhydride.}}{C^5H^4O^3}.$$

The acetone and carbonic oxide observed in an earlier stage of the decomposition are probably due to a secondary decomposition of aconitic acid, thus:

$$\underset{\text{Aconitic acid.}}{C^6H^6O^6} = 2CO^2 + CO + \underset{\text{Acetone.}}{C^3H^6O}.$$

Heated with *pumice*, citric acid gives off carbonic anhydride at 153° C.—4. Fused with *potash*, citric acid is decomposed into oxalic and acetic acids:

$$\underset{\text{Citric acid.}}{C^6H^8O^7} + H^2O = \underset{\text{Oxalic acid.}}{C^2H^2O^4} + \underset{\text{Acetic. acid.}}{2C^2H^4O^2}.$$

5. When citric acid is treated with strong *sulphuric acid*, a disengagement of carbonic oxide ensues, even without the application of heat. But if the temperature be raised the odour of acetone is perceived, and carbonic anhydride is given off. On adding carbonate of sodium to the residual liquid diluted with water, a brown resinous mass is precipitated, and the solution contains the sodium-salt of a peculiar acid, which does not precipitate baryta or strontia. — 6. Citric acid is not attacked by dilute *nitric acid;* but if heated for some time with strong nitric acid, it yields oxalic and carbonic acids.

7. Citric acid is easily oxidised by *permanganic acid.* A solution of citric acid mixed with sulphuric acid does not decolorise *permanganate of potassium* in the cold; but at 80° C. the citric acid is oxidised to carbonic acid and acetone:

$$2C^6H^8O^7 + H^2O + O^{10} = C^3H^6O + 9CO^2 + 6H^2O.$$

If a large excess of the permanganate be used, other products are likewise formed, namely, a body which strongly irritates the eyes and respiratory organs, reduces permanganate of potassium at common temperatures, and is turned brown by alkalis, probably therefore acrolein, together with an acid closely analogous to acrylic acid. Finely divided peroxide of manganese acts in the same way as the permanganate. (Péan de Saint Gilles, Ann. Ch. Phys. [3] lv. 374.)

8. *Chlorine* acts but feebly on citric acid. When a layer of concentrated solution of citric acid is exposed to the sunlight in a large globe filled with chlorine, the gas is slowly absorbed, and an oil gradually separates, which after rectification is colourless, has a sweetish burning taste, and a peculiar odour. It boils at 200°—201° C., and does not solidify at 0°. It reddens litmus paper only after prolonged contact. Plantamour, the discoverer of this body, assigns to it the formula $C^8Cl^{10}O^3$; when it is agitated with water and cooled to + 6°, a mass of crystals is formed, $C^8Cl^{10}O^3.3H^2O$, which melt and give off their water at 15°. The oil is attacked by potash, with formation of a body, $C^4Cl^4K^2O^4$. Städeler considers the oil to be hexachlorinated acetone C^3Cl^6O (p. 30), and the crystals to be a hydrate, $C^3Cl^6O + H^2O$. Laurent ascribes to the oil the formula $C^5Cl^{10}O^2$.

9. The action of chlorine on citrate of sodium, though not very energetic even in sunshine, is different. Carbonic acid is disengaged, and the liquor becomes milky from formation of an oil; at the same time, an acid citrate of sodium is formed, which crystallises in stellate groups. The odour of the oil, at first sweetish, becomes gradually more acrid. It is a mixture of several bodies. On rectification, chloroform first distils over at 64°—66° C.; the boiling point then rises to 188°—190°, and remains constant for some time; it then rises to 200°, at which point the oil produced by the free acid distils over. The intermediate product, on rectification, boils at 190°. It is a colourless and very fluid oil, of specific gravity 1·66, with a burning taste, an extremely irritating odour, and exciting tears. It has the formula $C^6Cl^{10}O^3$. The action of alcoholic potash on this oil yields chloride of potassium, and a very soluble potassium-salt which crystallises in satiny scales; it has the formula $C^4Cl^4K^2O^4$. The same salt is produced by the action of potash on the oil from the free acid. A corresponding silver-salt is very unstable, and is readily reduced to the metallic state even in the cold. The potassium-salt has the composition of that of a chlorinated succinic acid. The mother-liquor from which the chlorinated oil has been deposited contains, besides chloride of sodium, the sodium-salt of an acid which has the composition of succinic acid but appears to be only isomeric with it.

10. When *bromine* is gradually added to solution of citrate of potassium, a brisk disengagement of carbonic acid takes place; and if the addition of bromine be continued as long as gas is given off, and the excess of bromine carefully removed by potash, an oil is precipitated which is a mixture of two bodies. The most volatile of these is bromoform, $CHBr^3$. The other has received from Cahours the name bromoxaform. It consists of lustrous silky needles, which by spontaneous evaporation crystallise in large colourless plates. They melt between 74° and 75° C., but are gradually decomposed by distillation. The formula of the body is $C^3HBr^5O^2$ (pentachlorinated pro-

pionic acid): it is decomposed by potash, with formation of bromide of potassium, oxalic acid, and bromoform:

$$\underset{\text{Bromoxaform.}}{C^3HBr^5O^2} + 2KHO = 2KBr + \underset{\text{Oxalic acid.}}{C^2H^2O^4} + \underset{\text{Bromoform.}}{CHBr^3}.$$

11. Dried citric acid in contact with *pentachloride of phosphorus*, becomes heated, and yields oxychlorocitric acid and oxychloride of phosphorus:

$$C^6H^8O^7 + PCl^5 = C^6H^8O^6Cl^2 + POCl^3.$$

If the mixture be heated, hydrochloric acid is evolved, and chloride of citryl appears to be formed:

$$C^6H^8O^6Cl^2 + PCl^5 = \underset{\text{Chloride of citryl.}}{C^6H^5O^4Cl^3} + POCl^3 + HCl + H^2O.$$

If the heat be continued, the liquid assumes a deep cherry-red colour and then appears to contain chloride of aconityl:

$$C^6H^5O^4Cl^3 + PCl^5 = \underset{\text{Chloride of aconityl.}}{C^6H^3O^3Cl^3} + POCl^3 + 2HCl.$$

Citrates. Citric acid is a strong acid. It reddens blue litmus paper and expels carbonic acid from carbonates. An aqueous solution dissolves zinc and iron, with disengagement of hydrogen.

Citric acid is tribasic. It may be derived from 3 at. water in which 3 at. hydrogen are replaced by the triatomic radical citryl, $C^6H^5O^4$. It therefore forms three series of salts, in which 1, 2, or 3 at. hydrogen are replaced by metal, thus:—

Citric acid	$\left.\begin{matrix}(C^6H^5O^4)''' \\ H^3\end{matrix}\right\}O^3$
Acid monometallic citrate	$\left.\begin{matrix}(C^6H^5O^4)''' \\ H^2.M\end{matrix}\right\}O^3$
Acid dimetallic citrate	$\left.\begin{matrix}(C^6H^5O^4)''' \\ H.M^2\end{matrix}\right\}O^3$
Neutral trimetallic citrate	$\left.\begin{matrix}(C^6H^5O^4)''' \\ M^3\end{matrix}\right\}O^3$

Some of the citrates occur naturally, as citrate of calcium in onions and potatoes, and citrate of potassium in artichokes and potatoes. The alkaline citrates are very soluble; other citrates, as those of zinc, iron, cobalt and nickel are less so, while the citrates of the alkaline earths are insoluble. In the presence of soluble citrates, alkalis do not precipitate the salts of iron, manganese, or aluminium. The citrates decompose when heated to 230°C., forming empyreumatic products, which have not been investigated.

The following list includes all the principal citrates.

CITRATE OF ALUMINIUM.—Insoluble powder when it contains excess of metal; soluble gum when the acid is in excess.

CITRATE OF AMMONIUM. *Monammonic Citrate*, $C^6H^7(NH^4)O^7$.—Solution of citric acid, neutralised with ammonia, and then mixed with twice as much acid as it already contains, yields this salt by spontaneous evaporation in small triclinic prisms.

Diammonic Citrate, $C^6H^6(NH^4)^2O^7$, crystallises on the evaporation of a solution of citric acid which has been saturated by ammonia, in prisms which are anhydrous but deliquescent.

CITRATES OF BARIUM. *Tribarytic Citrate*, $C^6H^5Ba^3O^7$.—Citric acid added to excess of baryta-water throws down flakes which become somewhat crystalline. White powder; dried in the cold, it contains water of crystallisation, which it gives off completely at 200° C.

Monobarytic Citrate?—Obtained as a gummy mass by evaporating a solution of barytic citrate in citric acid.

A crystalline citrate of barium which, dried at 160° C., has the formula $C^{12}H^{11}Ba^5O^{14}$, is obtained by adding tribarytic citrate to a boiling transparent mixture of citric acid and chloride of barium, as long as the resulting precipitate redissolves, and then allowing the mixture to cool. It appears to be a double salt of tribarytic and dibarytic citrate.

Citrate of sodium is precipitated only by a large excess of chloride of barium: hence citrate of barium must be somewhat soluble in citrate of sodium.

CITRATE OF CADMIUM.—Crystalline sparingly soluble salt.

CITRATES OF CALCIUM. *Tricalcic Citrate*, $C^6H^5Ca^3O^7 + 2H^2O$.—When chloride of calcium is gradually added to a solution of citrate of sodium, the precipitate at first formed redissolves, but when agitated, it suddenly forms a magma which becomes crystalline on the application of heat. The salt is more soluble in cold than in hot water, so that a cold solution becomes turbid on being boiled.

Dicalcic Citrate, $C^6H^6Ca^2O^7 + H^2O$.—Obtained in shining laminæ by dissolving the preceding compound in excess of citric acid, and evaporating the solution.

Citrate of Cerium.—White insoluble powder, obtained by double decomposition of alkaline citrates and cerous salts.

Citrate of Cobalt, $C^6H^5Co^3O^7 + 7H^2O$.—The solution of carbonate of cobalt in warm citric acid, solidifies on cooling, after adequate evaporation, to a rose-coloured magma, which dries up to a powder of the same colour.

Cupric Citrate.—Obtained in microscopic rhombohedra by heating a solution of cupric acetate with citric acid. The formula is $C^6H^5Cu^3O^7.CuHO + H^2O$.

Citrates of Iron. *Ferrous Citrate.*—Alcohol precipitates white flakes of triferrous citrate from a clear solution of iron in citric acid.

Ferric Citrate.—Freshly precipitated hydrated ferric oxide dissolves in warm aqueous citric acid, forming a reddish-brown liquid which on evaporation leaves a light-brown film. It is administered medicinally under this form. Ferrocyanide of potassium does not precipitate an acid solution of ferric citrate, but forms a blue liquid which is decolorised by ammonia.

Ammonio-ferric Citrate. (Ammonio-citrate of iron.)—When 2 pts. of freshly precipitated ferric hydrate are dissolved in 3 pts. of citric acid, the solution saturated with ammonia leaves on evaporation a greenish-yellow mass, insoluble in strong alcohol, but soluble in alcohol of 40 per cent.

Citrate of Lithium.—Amorphous, limpid, hard mass.

Citrates of Lead. *Triplumbic Citrate*, $C^6H^5Pb^3O^7$ (at 120° C.), is best obtained by precipitating an alcoholic solution of plumbic acetate with an alcoholic solution of citric acid, and washing the precipitate with alcohol; it is granular when hot solutions are employed.

Diplumbic Citrate. $C^6H^6Pb^2O^7 + H^2O$.—A solution of acetate of lead is added to a boiling dilute solution of citric acid as long as the precipitate redissolves. On evaporating the clear solution, the salt crystallises in small prisms. Ammonia dissolves this salt, and the solution afterwards deposits triplumbic citrate.

Tetrabasic Salt.—By digesting triplumbic citrate with ammonia, Berzelius obtained a heavy white powder, which had the formula $C^6H^5Pb^3O^7.PbHO$, or $C^{12}H^5Pb^3O^{11}.PbO + HO$). The triplumbic citrate digested with excess of subacetate of lead, gave an insoluble amorphous powder, which had the formula $C^6H^5Pb^3O^7.PbHO.Pb^2O$ (or $C^{12}H^5Pb^3O^{11}.3PbO + HO$). Heldt obtained a salt of the formula $2(C^6H^5Pb^3O^7.Pb^2O) + 3H^2O$, or $C^{12}H^5Pb^3O^{11}.2PbO + 3HO$, by digesting triplumbic citrate with ammonia for two days in a close vessel. Bulky, white, insoluble powder

Citrate of Magnesium. $C^6H^5Mg^3O^7 + 7H^2O$.—Carbonate of magnesium dissolves in citric acid to a solution which forms a thick magma when concentrated. Alcohol precipitates the salt from its aqueous solution.

This salt, evaporated with excess of citric acid, yields a gummy mass, which does not become crystalline.

When carbonate of magnesium is digested with disodic citrate, the filtered solution on evaporation leaves small crystalline groups, which contain sodium and magnesium.

Citrate of Manganese. $C^6H^6Mn^2O^7 + H^2O$.—Citrate of sodium does not precipitate manganous salts; but when carbonate of manganese is digested with citric acid, the above salt is obtained as a white insoluble crystalline powder.

Citrates of Mercury.—Citric acid precipitates from *mercurous* acetate, a white powder soluble in nitric acid.

Freshly precipitated *mercuric oxide* dissolves in hot citric acid, and the solution on cooling deposits a white powder, which is decomposed by water.

Citrate of Nickel. $C^6H^5Ni^3O^7 + 7H^2O$.—Oxide of nickel dissolves in citric acid to a green liquid, gradually changing into a green jelly, which on evaporation leaves an olive-green film, soluble in water but precipitated by alcohol.

Citrates of Potassium. *Tripotassic Citrate.* $C^6H^5K^3O^7 + H^2O$.—A solution of carbonate of potassium neutralised with citric acid, yields by spontaneous evaporation, transparent, stellate-grouped needles, very deliquescent, and insoluble in absolute alcohol. They lose their water of crystallisation at about 200° C.

Dipotassic Citrate. $C^6H^6K^2O^7$.—A solution of 2 pts. of citric acid neutralised with carbonate of potassium, and mixed with 1 pt. of citric acid, yields by evaporation an amorphous mass having a sour taste.

Monopotassic Citrate. $C^6H^7KO^7 + 2H^2O$.—1 pt. of citric acid is neutralised with potash, 1 pt. of citric acid added, and the mixture evaporated at 40° C. Large transparent prisms, permanent in the air, and having an agreeable sour taste. They melt in their water of crystallisation, and give off 13·8 per cent. of water, forming a viscous liquid, which solidifies on cooling to a concentric radiated mass of crystals, consisting of $C^6H^7KO^7$.

Ammonio-potassic Citrate. $C^6H^5K^2(NH^4)O^7$.—A solution of dipotassic citrate neutralised with ammonia, yields this salt, on evaporation, in transparent deliquescent prisms.

Potassio-antimonic Citrate.—1 pt. of citric acid is neutralised with potash; 1 pt. more of acid added; the mixture boiled for some time with trioxide of antimony, and the filtrate left to crystallise. White, shining, very hard prisms, grouped in tufts. They give off 6·7 per cent. of water at 190° C. May be regarded as a double molecule of tripotassic citrate, in which part of the potassium is replaced by the tribasic radicle, antimony: $C^{12}H^{10}(K^3Sb''')O^{14}$.

CITRATE OF SILVER. $C^6H^5Ag^3O^7$.—Citrate of potassium added to solution of nitrate of silver, throws down this salt as a heavy white powder, which crystallises from boiling water in white or yellowish needles. Deflagrates at a high temperature.

Argentous Salt.—The above salt heated to 100° C. in a current of hydrogen, is changed into a dark brown mass, which is a mixture of citric acid and triargentous citrate. Water extracts from this mass first citric acid, and then a small quantity of argentous salt with a red colour. This red solution heated to boiling, assumes a green and blue colour, then deposits metallic silver, and becomes decolorised.

CITRATES OF SODIUM. *Trisodic Citrate.* $2(C^6H^5Na^3O^7) + 11H^2O$.—When a solution of citric acid is saturated with soda, and the solution left to evaporate, large rhombic prisms are obtained of this composition. They quickly effloresce and are sparingly soluble in alcohol. At 100° C. 7 at. water are given off, and at 190°—200°, 4 at. more. A solution of this citrate evaporated at 60° C., yields monoclinic crystals containing only 2 at. water.

Disodic Citrate. $C^6H^6Na^2O^7.H^2O$.—Obtained like the corresponding potassium-salt. Prismatic, stellate-grouped crystals, which give off their water of crystallisation when dried over oil of vitriol.

Monosodic Citrate. $C^6H^7NaO^7 + H^2O$.—Obtained like the corresponding potassium-salt. A very concentrated solution left to evaporate in a warm place, solidifies to a mass of acicular crystals, and crystallises to the last drop.

Ammonio-sodic Citrate.—Confused crystalline crust.

Potassio-sodic Citrate. $C^6H^5Na^3O^7.C^6H^5K^3O^7 + 11H^2O$—Obtained by dissolving equivalent quantities of trisodic citrate and tripotassic citrate, and concentrating by evaporation. It is deposited after some days in radiate-grouped, lustrous needles.

CITRATE OF STRONTIUM.—Strontia-water is precipitated by citric acid in thick white flakes, which, after drying over oil of vitriol, have the composition $C^6H^5Sr^3O^7 + H^2O$. They lose their water of crystallisation at 210° C.

CITRATE OF ZINC. $C^5H^5Zn^3O^7 + H^2O$.—Carbonate of zinc dissolves readily in aqueous citric acid; on boiling, the salt is precipitated as a granular, crystalline powder. The aqueous solution of this salt mixed with a small quantity of citric acid, and evaporated at a gentle heat, deposits transparent crystals, which have the composition $C^6H^5Zn^3O^7.C^6H^6Zn^2O^7 + H^2O$.

Substitution-derivative of Citric Acid.

OXYCHLOROCITRIC ACID. $C^6H^6Cl^2O^6 = \left.\begin{matrix}(C^6H^5O^4)'''\\H^3\end{matrix}\right\}\begin{matrix}Cl^2\\O^2\end{matrix}$.—When pentachloride of phosphorus is mixed with dry citric acid, the mass becomes heated, liquefies, and then solidifies to a magma of crystals which consist of oxychlorocitric acid mixed with oxychloride of phosphorus. The latter is removed by digestion with disulphide of carbon, the mass is thrown on a filter, and washed with disulphide, then pressed between bibulous paper, and dried in a current of hot air. It forms colourless silky needles:

$$C^6H^8O^7 + \acute{P}Cl^5 = C^6H^6O^6Cl^2 + POCl^3.$$

In moist air or in water, this acid becomes heated and is converted into citric acid.

On heating it in a stream of dry air to 100° C., hydrochloric acid is liberated, and the residue consists of aconitic acid. Dry ammonia acts violently upon it, forming a black vesicular mass. In contact with aniline, the acid becomes strongly heated, and yields phenyl-aconitimide.

E. A.

CITRIC ACID, AMIDES OF. (Pebal, Ann. Ch. Pharm. lxxxii. 73; xcviii. 67.)—Of the amides of citric acid, bodies derived from ammonia by the replacement of hydrogen by the radicle citryl, only citramide is known; but many of the corresponding phenyl-compounds have been obtained by Pebal.

CITRAMIDE. $C^6H^{11}N^3O^4 = \left.\begin{matrix}(C^6H^5O^4)''' \\ H^3 \\ H^3\end{matrix}\right\}N^3$, is a crystalline compound, slightly soluble in water, obtained by the action of alcoholic ammonia on citrate of methyl or citrate of ethyl.

Phenylcitramide. Citranilide. $\left.\begin{matrix}(C^6H^5O^4)''' \\ (C^6H^5)^3 \\ H^3\end{matrix}\right\}N^3$, is obtained by the action of heat on triphenylamic citrate:

$$\underset{\text{Triphenylamic citrate.}}{C^6H^5(C^6H^8N)^3O^7} - 3H^2O = \underset{\text{Phenylcitramide.}}{C^{24}H^{23}N^3O^4}.$$

To prepare this body, the yellow powder left on heating triphenylamic citrate is dissolved in boiling alcohol, and the solution is decolorised by animal charcoal. On cooling, two sets of crystals are deposited, hexagonal plates and fine prisms. The former consist of phenylcitrimide, and are dissolved out by boiling with alkali, which does not perceptibly affect the phenylcitramide. Phenylcitramide is deposited from alcohol in colourless prisms, truncated longitudinarily, and with a nacreous lustre. Neutral to vegetable colours.

Phenylcitrimide. Citrobianil. $C^{18}N^2H^{16}O^4 = \left.\begin{matrix}(C^6H^5O^4)''' \\ (C^6H^5)^2 \\ H\end{matrix}\right\}N^2$, represents diphenylamic citrate *minus* 3 atoms of water:

$$\underset{\text{Diphenylamic citrate.}}{C^6H^6(C^6H^8N)^2O^7} - 3H^2O = \underset{\text{Phenylcitrimide.}}{C^{18}H^{16}N^2O^4}.$$

It is obtained in the preparation of phenylcitramide; also by heating phenylcitramic acid with phenylamine:

$$\underset{\text{Phenylcitramic acid.}}{C^{12}H^{11}NO^5} + \underset{\text{Phenylamine.}}{C^6H^7N} = \underset{\text{Phenylcitrimide.}}{C^{18}H^{16}N^2O^4} + H^2O.$$

Hexagonal plates, soluble in alcohol, and converted by boiling with ammonia into diphenylcitramic acid.

Phenylcitramic Acid. Citranilic Acid. $C^{12}H^{11}NO^5 = \left.\begin{matrix}N(C^6H^5)(C^6H^5O^4)''' \\ H\end{matrix}\right\}O$.—Obtained by the action of heat on monophenylamic citrate:

$$\underset{\text{Monophenylamic citrate.}}{C^6H^7(C^6H^8N)O^7} - 2H^2O = \underset{\text{Phenylcitramic acid.}}{C^{12}H^{11}NO^5}.$$

Monophenylamic citrate is heated to 140° — 150° C. as long as water is given off. On cooling, the residue becomes crystalline. It dissolves readily in water, and if excess of phenylamine has been avoided, it is deposited in small crystalline spherules, or in mamillary groups of small prisms. It has an acid reaction, and forms crystalline salts with silver and with aniline.

On treating it with pentachloride of phosphorus, hydrochloric acid is given off, and a liquid formed, which appears to contain *chloride of aconitanyl*, $C^{12}NH^8O^3.Cl$, as, when treated with water, it is resolved into hydrochloric acid and phenylaconitamic acid.

Diphenylcitramic Acid. Citrobianilic Acid. $C^{18}H^{18}N^2O^5$.—Obtained in the form of an ammonia-salt by boiling phenylcitrimide with ammonia. By adding hydrochloric acid to the solution, the acid is precipitated. Recrystallised from alcohol, it forms soft, concentrically-grouped, silky needles. It melts and gives off water at 150° C., and becomes reconverted into phenylcitrimide.

Diphenylcitramic acid contains the elements of diphenylamic citrate *minus* 2 at. water: $C^6H^6(C^6H^8N)^2O^7 - 2H^2O = C^{18}H^{18}N^2O^5$, and may be represented by the formula $\left.\begin{matrix}(C^6H^5)^2 \\ (C^6H^5O^4)''' \\ H^3\end{matrix}\right\}\begin{matrix}N^2 \\ O\end{matrix}$, derived from the mixed type $N^2H^6.H^2O$. E. A.

CITRIC ETHERS. The citric ethers represent citric acid in which one or more atoms of hydrogen are replaced by alcohol-radicles. Those in which one or two atoms of hydrogen are thus replaced have acid properties.

Citrate of Methyl. *Trimethylic Citrate.* $C^9H^{14}O^7 = \left.\begin{matrix}(C^6H^5O^4)'''\\(CH^3)^3\end{matrix}\right\}O^3$.—A solution of citric acid in wood-spirit is saturated with hydrochloric acid gas; on rectifying the mixture, chloride of methyl and the excess of wood-spirit pass off, and a colourless liquid distils over at about 90° C., which is citrate of methyl. After standing some time it crystallises. (Saint-Èvre, Compt. rend. xxi. 144.)

Monomethylcitric Acid, $\left.\begin{matrix}(C^6H^5O^4)'''\\H^2.CH^3\end{matrix}\right\}O^3$, and *Dimethylcitric acid*, $\left.\begin{matrix}(C^6H^5O^4)'''\\H.(CH^3)^2\end{matrix}\right\}O^3$, are both formed in the preparation of citrate of methyl. They have been but little examined. (Demondesir, Compt. rend. xxxiii. 227.)

Citrate of Ethyl. *Citric Ether.* $\left.\begin{matrix}(C^6H^5O^4)'''\\(C^2H^5)^3\end{matrix}\right\}O^3$. (Thénard, Mém. d'Arcueil, ii. 12.—Malaguti, Ann. Ch. Phys. lxiii. 197.—Dumas, Compt. rend. viii. 528.—Marchand, J. pr. Chem. xx. 318.—Heldt, Ann. Ch. Pharm. xlvii. 57.—Demondesir, *loc. cit.*)—This body is formed by distilling a mixture of sulphuric acid, citric acid, and alcohol; but the best method of preparing it, according to Demondesir, is as follows: A solution of citric acid in alcohol is saturated with hydrochloric acid gas, the liquid neutralised with carbonate of soda, and agitated with common ether, which dissolves out the citric ether. On evaporating the ethereal solution, citric ether is left as an oily, yellowish, transparent liquid, with an odour resembling olive oil. Its specific gravity is 1·142. It is very soluble in alcohol and in ether. It boils at 280° C., but decomposes—probably into aconitic or citraconic ether. It is decomposed by free alkalis into citrates and free alcohol. With ammonia it yields, besides citramide, several products which have not been examined. E. A.

CITRIDIC ACID. Syn. with Aconitic Acid.

CITRILENE. See Citrene.

CITRINE. A glassy variety of quartz having a wine-yellow colour.

CITRINS. *Citroglycerins. Citrates of Glyceryl.* (van Bemmelen, J. pr. Chem. lxix. 84.)—Two of these compounds have been obtained by heating citric acid with glycerin.

Neutral Citrate of Glyceryl, $C^9H^{10}O^7 = \left.\begin{matrix}(C^6H^5O^4)'''\\(C^3H^5)'''\end{matrix}\right\}O^3$, is prepared by heating citric acid with a slight excess of glycerin to 160°—170° C. for twenty hours. Water then escapes, and there remains a hard, light yellow, transparent mass, from which the pure product may be obtained by boiling out the excess of glycerin with alcohol. It is difficult to pulverise; insoluble in water, alcohol, and ether. Hydrochloric acid dissolves it gradually with aid of heat; sulphuric acid immediately, with blackening. It dissolves gradually in cold potash-ley, and when boiled with bases, is quickly resolved into citric acid and glycerin. The formation of the compound is represented by the equation:

$$\underset{\text{Citric acid.}}{C^6H^8O^7} + \underset{\text{Glycerin.}}{C^3H^8O^3} = C^9H^{10}O^7 + 3H^2O.$$

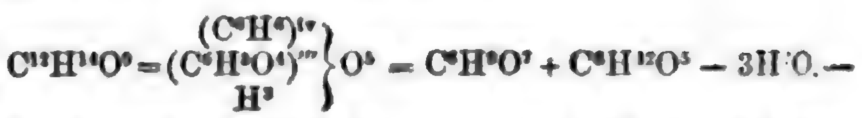
Basic Citrate of Glyceryl. Citrodiglyceride, $C^{12}H^{18}O^{10} = C^9H^{10}O^7.C^3H^8O^3$, may be regarded as a double molecule of glycerin $\left(\left.\begin{matrix}C^6H^{10}\\H^6\end{matrix}\right\}O^6\right)$, in which 3 at. hydrogen are replaced by citryl, that is to say, as $\left.\begin{matrix}(C^6H^{10})^{vi}\\(C^6H^5O^4)'''\\H^3\end{matrix}\right\}O^6$.—Obtained like the preceding, by heating citric acid with a double quantity of glycerin. The mass melts at 100° C., and the transformation is completed between 160° and 170°. The product purified by boiling with alcohol, is yellowish-brown, somewhat darker and less hard than the neutral compound, which, however, it resembles in other respects.

CITROCERIC and **CITROLIC ACIDS.** Two acids said to be contained in the sediment of lemon and bergamot oils; the former is waxy, the latter oily. (Mylius, Arch. Pharm. xxxii. 28.)

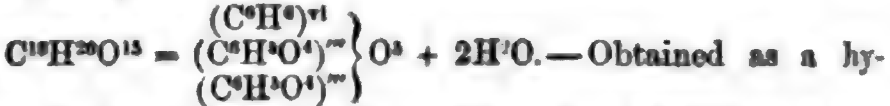
CITRODIANIL. Syn. with Phenylcitrimide (p. 998).

CITROGLYCERIN. See Citrins.

CITROMANNITANS. (v. Bemmelen, Jahresber. f. Chem. 1858, p. 435.)—This term is applied to two compounds derived from mannite in the same manner as the citrins are derived from glycerin. They are formed by heating citric acid with mannite in proper proportion to between 130° and 140° C., combination then taking place, attended with elimination of water.



Monocitromannitan. $C^{12}H^{14}O^{9} = \left.\begin{matrix}(C^{6}H^{8})^{iv}\\(C^{6}H^{5}O^{4})'''\\H^{3}\end{matrix}\right\}O^{5} = C^{6}H^{8}O^{7} + C^{6}H^{12}O^{5} - 3H^{2}O$.— A hard, light yellow, tasteless substance, insoluble in cold water, alcohol, and ether, decomposed by long boiling with water or alcohol, also by alkalis. Between 170° and 180° C. it turns brown and decomposes.



Dicitromannitan. $C^{18}H^{20}O^{15} = \left.\begin{matrix}(C^{6}H^{8})^{vi}\\(C^{6}H^{5}O^{4})'''\\(C^{6}H^{5}O^{4})'''\end{matrix}\right\}O^{5} + 2H^{2}O$.—Obtained as a hydrate by heating 2 at. citric acid and 1 at. mannite for some time to between 140° and 150° C. The product is a dry, hard, light yellow mass, which has no acid reaction, dissolves in water only after long boiling, is easily decomposed by alkalis, and does not give off water without decomposition when heated.

CITRON, OIL OF. See CITRUS MEDICA (p. 1004).

CITRONYL. The name applied by Blanchet and Sell to that constituent of lemon-oil, which forms a crystallisable compound with hydrochloric acid (p. 1004). It is sometimes also applied to the triatomic radicle of citric acid.

CITROPTENE. The camphor or stearoptene of lemon-oil (p. 1004).

CITRUS. A genus of plants belonging to the natural order *Aurantiaceæ*, and including the orange, lemon, citron, shaddock, &c. They all produce juicy fruits containing citric acid, and enclosed in a thick fleshy rind containing volatile oils, which are isomeric with oil of turpentine, but differ from one another in odour, density, action on polarised light, &c.

CITRUS AURANTIUM. The *Sweet Orange.*—The rind of this fruit contains a volatile oil, *Oil of orange-peel, Oleum corticum aurantiorum*, which may be extracted by pressure or by distillation with water. It has the same composition and vapour-density as oil of lemon. Specific gravity in the liquid state 0·83—0·89. Boiling point 180° C. It is neutral, and has an agreeable odour. Optical rotatory power, 125·6°—127·4° to the right. It dissolves completely in absolute alcohol, and with turbidity in 7—10 pts. alcohol of specific gravity 0·85. It unites with hydrochloric acid, forming a liquid compound, $C^{10}H^{16}.HCl$, and a solid compound, $C^{10}H^{16}.2HCl$, which melts at 50° C. (Gm. xiv. 306.)

Orange-peel also contains, especially in the unripe state, a bitter principle called **Aurantiin** or **Hesperidin** (*q. v.*)

The juice of the orange contains citric and malic acids, partly free, partly combined with bases. The juices of sweet oranges likewise contains grape-sugar or cane-sugar; the grape-sugar predominates in the unripe state, but does not sensibly increase in quantity as the fruit ripens, while the amount of cane-sugar increases, both absolutely and relatively to the weight of the orange, the juice, and the solid constituents (Berthelot and Buignet, Compt. rend. li. 1094). 100 pts. of oranges contain 4·2 per cent. cane-sugar, 4·3 grape-sugar, and 0·45 free acid (Buignet, Ann. Ch. Phys. lxi. 233). The pips of the orange contain a bitter substance, which appears to be identical with the limonin of lemon-pips.

The flowers of the orange contain a very fragrant volatile oil, called *Oil of Neroli, Oleum florum naphæ s. neroli*, which is obtained by distilling the flowers with water. When recently prepared, it is nearly colourless, but reddens quickly on exposure to light. According to Soubeiran and Capitaine, it is composed of two oils, one easily soluble in water and very fragrant, while the other is sparingly soluble and has a less agreeable odour; the latter floats on the watery distillate, and is easily separated. The more fragrant oil may be extracted from the watery distillate (*orange-flower water*) by means of ether. It is reddened by *sulphuric acid*, and communicates this property to the entire essence. *Nitric acid* colours the oil brown. According to Döbereiner, oil of neroli produces a peculiar acid in contact with *platinum-black*. Oil of neroli dissolves clearly in 1—3 pts. *alcohol* of specific gravity 0·85, and with turbidity in a larger quantity. According to Boullay and Plisson, alcohol of 90 per cent. separates from oil of neroli a solid substance, neroli-camphor, melting at 50° C.; insoluble in water, sparingly soluble in boiling absolute alcohol; very soluble in ether; it appears to contain 83·76 per cent. C, 15·09 H, and 1·15 O; probably a hydrocarbon when pure. (Gm. xiv. 386; Gerh. iii. 639.)

The leaves of the orange yield a watery infusion characterised by a bitter aromatic taste.

The following table exhibits the composition of the ash of various parts of the orange-tree: —

Ash of Orange-tree.

	Rowney and Blow.					Richardson.
	Root.	Stem.	Leaves.	Fruit.	Pips.	Fruit.
Ash, per cent. . .	4·48	2·74	13·7	3·94	3·3	—
Potash	15·4	11·7	16·5	36·4	40 3	38·7
Soda	4·5	3·0	1·7	11·4	0·9	7·6
Lime	49·9	55·6	56·4	24·5	19·0	23·0
Magnesia . . .	6·9	6·3	5·7	8·0	8·7	6·5
Ferric oxide . . .	1·0	0·6	0·5	0·5	0·8	—
Sulphuric acid (anhydrous) . . .	5·8	4·6	4·4	3·7	5·1	2·9
Silicic acid (anhydrous)	1·7	1·2	4.8	04	1·1	5·2
Phosphoric acid „	13·5	17·1	3·3	11·1	23·2	14·1
Chloride of sodium .	1·2	0·2	6·6	3·9	6·8	trace
Ferric phosphate . .	—	—	—	—	—	1·7

Citrus Bergamia. *The Bergamot.*—The rind yields by pressure a volatile oil, $C^{10}H^{16}$, which deposits by keeping, a solid camphor called bergaptene, having the composition C^3H^2O. (See Bergamot, Oil of, p. 580.)

Citrus Bigaradia. The *Bigarade* or *Bitter Orange* (*Bigaradier* of the French, *Melangolo* of the Italians).—The rind of the fruit of this plant yields by pressure a volatile oil, $C^{10}H^{16}$, commonly called *Oil* or *Essence of Mandarin* (though the mandarin orange is a variety of *Citrus aurantium*). After filtration, it has a pale yellowish colour, but after rectification it is colourless, clear, and mobile. Specific gravity, 0·852 at 10° C., 0·8517 at 12°. Boiling point 178°. It has an agreeable odour, different from that of lemon or orange-oil, and a not unpleasant taste, like that of orange-oil. Optical rotatory power 85·5° to the right. It is insoluble in *water*, but soluble in 10 pts. of *alcohol*, also in *ether* and *glacial acetic acid*, and in all proportions in *sulphide of carbon*. It dissolves *bromine*, *iodine*, *phosphorus*, *sulphur*, *oils* both fixed and volatile, *wax*, and *resins*. With *hydrochloric acid* it forms a crystalline compound containing $C^{10}H^{16}.2HCl$. Cold *nitric acid* colours it faintly yellow; hot nitric acid decomposes it, with evolution of nitrous fumes, and the mixture, on addition of water, deposits a nearly solid mass. With *alcoholic nitric acid*, it forms a crystalline mass, probably a hydrate. It is reddened by cold *sulphuric acid*, and carbonised when heated therewith. (S. de Luca, Compt. rend. xlv. 904.—Gm. xiv. 304.)

The Seville bigarade, or Seville orange, is much used for the preparation of bitter tinctures and of candied orange-peel. The bitter aromatic principle is a powerful tonic, and gives its flavour to the liquid called Curaçoa.

Citrus Limetta. The *Lime.*—The rinds when torn and pressed, or distilled with water, yield an oil which resembles oil of lemon, and when treated with sulphuric acid and chromate of potassium, forms limettic acid, $C^{11}H^8O^6$. (Gm. *loc. cit.*)

Citrus Limonum. The *Lemon.*—Regarded by many writers as a variety of *Citrus medica.*

Lemon-juice contains free citric acid, and is used for the preparation of that acid (p. 902), also mucus, vegetable albumin, and sugar; according to Buignet (Ann. Ch. Phys. [3] lxi. 233), 100 pts. of it contain 1·1 grape-sugar, 0·4 cane-sugar, and 4·7 free acid. The nitrogenous matter causes it to putrefy easily, whence it acquires an unpleasant smell and taste; to prevent this change, it is often kept in bottles, with a layer of oil on its surface.

According to Witt (Chem. Soc. Qu. J. vii. 44), lemon-juice contains from 0·2 to 0·5 per cent. ash, consisting in 100 pts. of 44·3 per cent. potash, 2·1 soda, 7·6 lime, 3·3 magnesia, 12·5 sulphuric anhydride, 19·7 carbonic anhydride, 7·6 phosphoric anhydride, 1·0 ferric phosphate, 1·2 chlorine, and 0·6 silica.

Lemon-pips contain in the nucleus, citrate of potassium, a fatty non-drying oil, a tallow-like fat, a bitter principle called *limonin*, together with other constituents.

In the ash of lemon-pips, Souchay (J. pr. Chem. xxxviii. 25) found 33·2 per cent. potash, 3·5 soda, 12·6 lime, 8·5 magnesia, 0·2 ferric oxide, 34·1 phosphoric anhydride, 3·2 sulphuric anhydride, 2·3 chloride of sodium, and 0·3 silica.

Oil of Lemon.—Lemon-peel contains a volatile oil, called *Oil of lemon*, *Oleum citri*, which is extracted by pressure or by distillation with water. This oil is composed for the most part of a hydrocarbon isomeric with oil of turpentine, $C^{10}H^{16}$, and having the same vapour-density (4·81—4·87). It is neutral, and has an agreeable odour. Specific gravity in the liquid state, 0·84—0·86 (Zeller). Boiling point 173° C. (Blanchet and Sell); 176·1° (Brix). It volatilises in the air at ordinary temperatures without leaving a perceptible grease-spot, provided it has not become resinous by oxidation. It deflects the plane of polarisation of light to the right.

Oil of lemon, obtained as above, is, however, a mixture of two hydrocarbons, having the same composition, but differing in optical rotatory power and in their behaviour with hydrochloric acid. These two hydrocarbons may be separated by distilling the oil in vacuo. The first portions collected at 55° C. have a density of 0·8514 at 15° C., rotatory power = + 56·4°, and when saturated with hydrochloric acid gas, yield a solid and a liquid dihydrochlorate. The following portions collected at about 80° C. have a specific gravity of 0·8506 at 15°, rotatory power = + 72·5°, and are almost wholly transformed by hydrochloric acid into a solid dihydrochlorate; they likewise contain a sensible amount of oxidised oils. (Berthelot.)

Oil of lemon dissolves sparingly in *water*, in 7·14 pts. *alcohol* of specific gravity 0·8317, in 10 pts. alcohol of specific gravity 0·85, in any quantity of absolute alcohol, and mixes readily with *oils* both fixed and volatile. It dissolves *sulphur* and *phosphorus*, also *resins* and other bodies.

Oil of lemon when exposed to *air* and *light*, absorbs oxygen, with formation of ozone, becoming at the same time darker and more viscid, and forming a small quantity of carbonic acid; according to Aschoff, the crude, but not the rectified oil, turns acid on exposure to the air, forming acetic acid and lemon-camphor. At a *red heat*, the oil is decomposed, with formation of tar and charcoal. *Chlorine* decomposes it; cotton soaked in the oil and immersed in chlorine gas becomes charred on the surface, but does not take fire. When *bromine* is covered with a layer of water, the water with oil of lemon, and the whole carefully mixed, the bromine becomes decolorised without explosion, and a brominated oil is formed, 1 pt. of rectified lemon-oil taking up 2·28 pts. and 1 pt. of the crude oil, 2·4 to 2·5 pts. of bromine (G. Williams, Chem. Gaz. 1853, p. 365). *Iodine* decomposes oil of lemon with rise of temperature. Strong *nitric acid* turns it brown and resinises it; alcoholic nitric acid converts it into a hydrate. With strong *sulphuric acid*, it assumes a yellowish brown colour, and yields terebene and colophene; similarly when distilled with *phosphoric anhydride*. Lemon-oil dropped into a large quantity of oil of vitriol is said to yield sulphoterebic acid (Gerhardt). *Potassium* eliminates hydrogen from lemon-oil, slowly at common temperatures, more quickly when heated, acquiring at the same time a brown colour; after repeated distillation over potassium, however, the oil undergoes no further alteration, and then possesses a finer odour than before. *Hydrate of potassium* separates from oil of lemon a brown substance, the oil thereby acquiring a stronger and more agreeable odour.

Oil of lemon is largely used in perfumery; it should not be dark coloured or viscid or leave a perceptible stain on paper. It is often adulterated with cheaper oils, such as oil of turpentine or oil of lavender, and sometimes with alcohol. The latter adulteration may be detected by agitation with water, the pure oil then exhibiting no perceptible diminution of volume. The pure oil is also coloured brownish by acid chromate of potassium, whereas if it contains alcohol, it turns greenish.

The admixture of cheaper oils may generally be detected by the odour. Oil of turpentine may also be detected in oil of lemon by its different behaviour to polarised light, especially when heated, the molecular constitution of oil of lemon being much less altered by heat than that of oil of turpentine. The rotatory power of the suspected oil is first to be determined at the ordinary temperature, and again after the oil has been heated to 300° C. for an hour or two. If the oil is pure, no change will be perceived, but if oil of turpentine is present, especially the French kind, which is lævo-rotatory, the dextro-rotatory power of the oil will be considerably increased by the heating.

Hydrate of Lemon-oil is a crystalline substance isomeric with hydrate of turpentine-oil, $C^{10}H^{16}.2H^2O$, obtained by mixing 1 pt. of lemon-oil with $\frac{3}{4}$ pt. alcohol, of specific gravity 0·85, and $\frac{1}{4}$ pt. ordinary nitric acid, and leaving the mixture to itself for some time. (Deville.)

Hydrochlorates of Lemon-oil.—These compounds are formed by saturating the oil with hydrochloric acid gas, also by treating the oil with the aqueous acid. The compound formed in largest quantity is the *dihydrochlorate*, $C^{10}H^{16}.2HCl$, of which there is a solid and a liquid modification, the latter being produced chiefly from the more volatile, the former from the less volatile portion of the oil. (Berthelot, *vid. sup.*)

Monohydrochlorate. $C^{10}H^{16}.HCl$.—This compound is produced by saturating a solution of lemon-oil in acetic acid or alcoholic sulphuric acid, with hydrochloric acid gas, and collecting the few crystals which separate, rarely, however, and only under peculiar circumstances. It appears also to be present in small quantity in the portion of lemon-oil which remains liquid after the separation of the solid dihydrochlorate. The crystals melt at 100° C., and volatilise without decomposition at higher temperatures.

Dihydrochlorate. $C^{10}H^{16}.2HCl$.—The solid modification of this compound is obtained by passing dry hydrochloric acid gas to saturation into rectified and dehydrated oil of lemon well cooled, separating the resulting crystals from the mother-liquor, pressing them repeatedly between paper, washing them with cold alcohol, recrystallising from hot alcohol, drying in the air, afterwards in vacuo or over oil of vitriol, and once more crystallising from ether (Blanchet and Sell). It forms right four-sided prisms or laminæ, heavier than water; has an aromatic odour; is insoluble in water, soluble at 14° C. in 5·88 pts. of alcohol of specific gravity 0·806; and separates from the solution, on addition of water, in crystalline laminæ. On evaporating the alcoholic solution, partial decomposition takes place. The crystals are also soluble in oils both fixed and volatile. The compound is optically inactive, melts at 43° or 44° C., and solidifies crystalline on cooling; it sublimes at 50° C. without decomposition, boils at 142° (Cahours), at 162° (Blanchet and Sell), with partial decomposition, hydrochloric acid escaping and an oil passing over, which does not solidify till cooled to 20° C. The crystals burn with difficulty when heated in the air. *Chlorine-gas* converts the fused compound, with rise of temperature, into a chlorinated compound, $C^{10}(H^{14}Cl^{2}).2HCl$, Laurent's *hydrochlorate de chlorocitrenèse.*

Dihydrochlorate of lemon-oil is decomposed by *silver* and *mercurous salts* in the cold, not by *oxide of lead*, even when heated. *Nitric acid* does not act upon it in the cold, but decomposes it when heated, with evolution of nitrous acid. *Strong sulphuric acid* decomposes it, separating hydrochloric acid. *Potassium* decomposes it, with separation of lemon-oil; if heat be applied, citrene (p. 992) is produced. The same product is obtained by repeated distillation of the compound with potash or lime, or by the action of those bases at high temperatures.

The liquid dihydrochlorate, called also *hydrochlorate of citrilene* and *hydrochlorate of citryl*, is contained in the mother-liquor of the preceding compound, and may be obtained pure by cooling the mother-liquor to −10° C. to separate the remaining quantity of the solid compound, and filtering through a mixture of chalk and animal charcoal, to remove free acid and colouring matter. It is a mobile oil, optically inactive, soluble in alcohol, and precipitated from the solution by water, with loss of hydrochloric acid. By treatment with hydrochloric acid gas, it is converted into a crystalline mass, which dissolves in alcohol, but separates therefrom, not in crystals, but in the form of a heavy oil, a small quantity remaining in solution.

Lemon-camphor or *Citroptene.*—A solid substance produced from lemon-oil by oxidation. It is formed when the oil is kept for some time in half-filled bottles, partly separating in the solid state, while the rest remains dissolved, and may be separated by rectifying the oil. It forms colourless volatile crystals, which smell like oil of lemon, have a sharp pungent taste, are neutral, insoluble in cold water, but very soluble in hot water, to which they impart a decided dichroïsm. It is soluble also in alcohol and ether, the hot saturated solutions solidifying on cooling. The compound melts at 46° C. (Mulder), above 100° (Berthelot), boils at a temperature above 100°, and distils in oil-drops, which solidify in the crystalline form; it may also be sublimed. When thrown on red-hot coals, it volatilises without taking fire. It dissolves in *sulphuric acid* with red colour and peculiar aromatic odour, and water precipitates from the solution a white resinous substance, which is insoluble in water, and does not melt at 100°. *Nitric acid* dissolves the camphor, with decomposition at common temperatures, but gives off nitrous acid when heated with it. The camphor does not absorb *hydrochloric acid.*

The composition of lemon-camphor is not known with certainty. According to Mulder, it contains 54·8 per cent. C, 9·2 H, and 36·0 O; according to Berthelot, 58·0 C, 7·5 H, and 34·5 O.

The term lemon-camphor is likewise applied to two other compounds, viz. the solid dihydrochlorate of lemon-oil, and the hydrate formed by the action of alcoholic nitric acid on the same oil.

CITRUS LUMIA. The *Sweet Lemon.*—This plant, which grows abundantly in Calabria and Sicily, yields a fruit very much like the common lemon. The rind yields by pressure a volatile oil, the greater part of which distils between 180° and 190° C. yielding a colourless limpid liquid.

The portion boiling at 180° is isomeric with oil of turpentine, &c., and has a density of 0·853 at 18°. It possesses a dextro-rotatory power = 34° for the transition-tint.

It is slightly soluble in *alcohol*, very soluble in *ether* and in *sulphide of carbon*. It is resinised by strong *nitric acid*, and, like oil of lemon, yields a crystalline hydrate with alcoholic nitric acid. With *hydrochloric acid*, it forms a liquid and a crystalline compound; the latter, which has a peculiar odour and melts a low temperature, is a *dihydrochlorate*, $C^{10}H^{16}.2HCl$. (S. de Luca, Compt. rend. li. 258.)

Citrus Medica. The *Citron*. (*Citradier* of the French, *Cedro* or *Cedrato* of the Italians.)—The fruit of this species is usually large, warted and furrowed, with an extremely thick spongy rind and a subacid pulp. It is chiefly valued for the fragrance of the rind, from which a delicate sweetmeat is prepared. Two volatile oils used in perfumery are extracted from it, viz. *oil of citron* and *oil of cedra*. Both are highly fragrant, almost colourless, and lighter than water; they are distinguished by their odour, that of oil of cedra partaking of the character of oil of bergamot. The two oils are often confounded by pharmaceutical writers. They appear to be obtained by distillation, as they are free from mucilage. Both of them are *hydrocarbons* isomeric with oil of turpentine. (Pereira, *Materia Medica*, 3rd ed. 1853, ii. 2032.)

CITRYL. This name is applied to the triatomic radicle, $C^6H^5O^4$, of citric acid, &c.; also by Blanchet and Sell to that portion of lemon-oil which forms a liquid compound with hydrochloric acid (p. 1002).

Chloride of citryl $(C^6H^5O^4)'''Cl^3$, appears to be formed, together with oxychlorocitric acid and chloride of aconityl, when citric acid is heated with pentachloride of phosphorus (p. 997), inasmuch as the mother-liquor which remains after the oxychlorocitric acid has crystallised out, yields, on addition of water, both citric and aconitic acids. (Pebal.)

The following is a list of the compounds of citryl described in preceding articles $[C^6H^5O^4 = Ci]$.

Chloride of Citryl . . .	$Ci'''Cl^3$	Citrate, diglyceric .	$\left.\begin{matrix}Ci'''\\2(C^3H^5)'''\\H^3\end{matrix}\right\}O^6$
Citric acid	$\left.\begin{matrix}Ci'''\\H^3\end{matrix}\right\}O^3$	Citromannitan . . .	$\left.\begin{matrix}Ci'''\\(C^6H^8)^{iv}\\H^3\end{matrix}\right\}O^3$
Citrates, monometallic . .	$\left.\begin{matrix}Ci'''\\H^2M\end{matrix}\right\}O^3$	Dicitromannitan . . .	$\left.\begin{matrix}Ci'''\\Ci'''\\(C^6H^6)^{iv}\end{matrix}\right\}O^3$
Citrates, dimetallic . . .	$\left.\begin{matrix}Ci'''\\HM^2\end{matrix}\right\}O^3$	Citramide	$\left.\begin{matrix}Ci'''\\H^3\\H^3\end{matrix}\right\}N^3$
Citrates, trimetallic . .	$\left.\begin{matrix}Ci'''\\M^3\end{matrix}\right\}O^3$	Phenylcitramide . .	$\left.\begin{matrix}Ci'''\\(C^6H^5)^3\\H^3\end{matrix}\right\}N^3$
Citrate, monomethylic . .	$\left.\begin{matrix}Ci'''\\CH^3\\H^2\end{matrix}\right\}O^3$	Phenylcitrimide . .	$\left.\begin{matrix}Ci'''\\(C^6H^5)^2\\H\end{matrix}\right\}N^3$
Citrate, dimethylic . .	$\left.\begin{matrix}Ci'''\\(CH^3)^2\\H\end{matrix}\right\}O^3$	Phenylcitramic acid . .	$\left.\begin{matrix}C^6H^5\\Ci'''\\H\end{matrix}\right\}\begin{matrix}N\\O\end{matrix}$
Citrate, trimethylic . .	$\left.\begin{matrix}Ci'''\\(CH^3)^3\end{matrix}\right\}O^3$	Diphinylcitramic acid . .	$\left.\begin{matrix}(C^6H^5)^2\\Ci'''\\H^3\end{matrix}\right\}\begin{matrix}N^2\\O\end{matrix}$
Citrate, triethylic . . .	$\left.\begin{matrix}Ci'''\\(C^2H^5)^3\end{matrix}\right\}O^3$		
Citrate, monoglyceric .	$\left.\begin{matrix}Ci'''\\(C^3H^5)'''\end{matrix}\right\}O^3$		

CIVET. An odoriferous substance obtained from animals of the genus *Viverra* (Cuv.), viz. the *Viverra civetta* of North Africa, *V. zibetha*, found on the continent of Asia, from Arabia to Malabar, and *V. Rasse* of Java. It is contained in a pouch situated between the anus and organs of generation, and is voided by the animals against shrubs or stones. A better quality is, however, obtained by keeping the animals in confinement, and squeezing the pouch at certain intervals.

Good civet is of a clear yellowish or brownish colour, not fluid, nor hard, but about the consistence of butter or honey, and uniform throughout, of a very strong smell, resembling musk or ambergris; quite offensive when undiluted, but agreeable when only a small portion of civet is mixed with a large quantity of other substances.

Civet unites with oils, but not with alcohol.

Boutron-Charlard states, that in an unexceptionably good civet, semi-fluid, unctuous and yellow, he found free ammonia, stearin, oleïn, mucus, resin, volatile oil, yellow colouring substance, and salts. No benzoic acid could be detected in it. (J. Pharm. 1824, p. 537.)

CLARIFICATION. Clarification is the process of freeing a liquid from heterogeneous matter or feculencies; the term is, however, seldom applied to the mere mechanical process of straining, for which see FILTRATION.— Albumin, gelatin, acids, certain salts, lime, blood, and alcohol, serve in many cases to clarify fluids, which cannot be freed from their impurities by simple percolation. Albumin or gelatin, dissolved in a small portion of water, is commonly used for fining vinous liquors, as it inviscates the feculent matter, and gradually subsides with it to the bottom. Albumin in the form of white of egg or serum of blood is particularly used for fluids with which it will combine when cold, as syrups; as it is coagulated by the heat, and then rises in a scum with the dregs.—Heat alone clarifies some fluids, as the juices of plants, in which, however, the albumin they contain is probably the agent.—A couple of handfuls of marl, thrown into the press, will clarify cider, or water-cider.

Very finely divided precipitates, which remain for a long time suspended in pure water, may often be made to settle down, by adding a soluble salt, such as salammoniac, to the water. The same addition greatly facilitates the filtering and washing of precipitates, which otherwise stop up the pores of the filter.

CLASSIFICATION. The object of a classification of chemical substances is the arrangement of them in such a way that the position in the system of each substance may express its own chemical nature and the relation in which it stands to other substances. Hence it is easy to see that a system of classification, which should be perfect, relatively to any given stage in the development of the science, would be an epitome of the whole mass of chemical knowledge existing at the time. Hitherto but slight advances have been made towards establishing a theory of the causes or essential nature of chemical action; our so-called chemical theories are, for the most part, attempts to express the mutual relations of a greater or lesser number of chemical substances; in reality, therefore, they are more or less comprehensive schemes of classification. A general system of chemical classification ought to embrace the fundamental principles of all such partial systems, so as to show the real nature and relative value of each: it ought, in fact, to be a general expression of these theories in much the same sense that they are general expressions of chemical facts. A discussion of the bases upon which a comprehensive classification is to be founded becomes therefore a discussion of chemical theories in general; and in this article we shall endeavour to set forth clearly those general results of chemical research, by reference to which the true value of all chemical theories must, in the present state of the science, be tested, and which must for the present, be taken as the foundation for any attempt at chemical classification, rather than to construct a detailed scheme of classification in which each individual substance should find its place.

A collection of complex objects can always be classified in several different ways, according as this or that quality is regarded as the most important. In the case of chemical substances, two causes are always at work to bring about changes of the point of view from which they are regarded with reference to their classification. In the first place, the number of objects to be classified is continually increasing through the discovery of new substances; and, in the second place, the finding out of new qualities in the bodies already known, tends continually to modify their apparent relations to each other. Hence it is not surprising that, instead of our being able to trace, in the history of chemistry, the gradual extension of one fundamental scheme of classification, we should find that the principles upon which it has been attempted to classify chemical substances have been gradually, but from time to time almost completely changed as the science has advanced. It is not necessary to consider here what these changes have been; we have only referred to their occurrence, in order to draw attention to the fact, that the most perfect classification which it is possible even now to give, can of necessity be nothing more than a representation of the results of chemical labour, as they appear viewed from the point which the science has now reached, and that it must hereafter be absorbed in some more general system, if it be not entirely set aside.

All chemical substances belong to one of two classes: namely, elements or simple bodies, and compound bodies. The chemical definition of an element is — a body which cannot be decomposed or shown to contain matter of more than one kind; compound bodies, on the other hand, are such as are made up of, or can be decomposed into, two or more distinct kinds of matter. For instance, water can be shown to contain two kinds of matter, called respectively oxygen and hydrogen; sugar can similarly be proved to be made up of oxygen, hydrogen and carbon; water and sugar are therefore both of them compound bodies; but neither oxygen, hydrogen, nor carbon can, by any analytical or *breaking-up* process, be made to yield anything else than oxygen, hydrogen, or carbon, respectively; these three bodies are therefore in a chemical sense, elements. It will be seen that the chemical idea of an elementary body does not by any means imply the absolute simplicity of the so-called elements; it may be that these bodies are compounds which, as yet, have resisted all attempts to decompose them, but which are capable of being decomposed by processes hitherto unknown. Nevertheless, if it should at some future time be shown that all our present elements are in reality compound bodies, the definition of elements as bodies which cannot be chemically decomposed would still hold good, though it would then be applicable to a new set of substances.

In the further classification of elementary and compound bodies, it is impossible to separate the consideration of one of these classes from that of the other; for the chemical nature of an elementary body can only be known by the study of the combinations which it forms; and the properties of every compound body are determined by those of the elements of which it is composed.

There are especially two points to be considered in reference to the relation in which the various elements stand to the compounds which they form: first, the atomic proportion in which they combine together; second, the chemical nature or function of the bodies into whose composition they enter. Considering them first in the former relation, we find that there are a certain number which are distinguished from all the rest by the simplicity of the proportion in which they unite with each other. To this class of elements belong hydrogen ($H = 1$), chlorine ($Cl = 35{\cdot}5$), bromine ($Br = 80$), iodine ($I = 127$), potassium ($K = 39$), sodium ($Na = 23$), lithium ($Li = 7$), rubidium ($Rb = 85{\cdot}4$), cæsium ($Cs = 133$), silver ($Ag = 108$).* They combine together usually in the proportion of one atom to one atom (see ATOMIC WEIGHTS), and but few compounds are known which contain more than two of these elements, unless an element of some other class be also present. Trichloride of iodine, ICl^3 †, and the supposed chloride of bromine, $BrCl^5$, are perhaps the only exceptions to the former of these rules, and the substances which form an exception to the second are all crystallised salts formed by the molecular union of normal binary compounds, such as NaCl and AgCl. These bodies cannot be proved to exist, except in the crystallised state, and the chemical properties of their two constituents are not modified to the extent which usually accompanies true chemical combination; hence it is probable that they are not true chemical individuals, but physical aggregates of entire molecules, analogous to salts containing water of crystallisation. Another property of the elements of this class, closely allied to the first that was mentioned, is that the proportion by volume in which those of them which can be measured in the gaseous state unite, is 1 : 1.

For reasons that will be further dwelt upon in the sequel, the elements of this class are termed *monatomic* elements; the remainder are termed *polyatomic* elements and are divisible into:

1. *Diatomic Elements.*—These are: oxygen ($O = 16$), sulphur ($S = 32$), selenium ($Se = 80$), tellurium ($Te = 128$), magnesium ($Mg = 24$), zinc ($Zn = 65$), cadmium, ($Cd = 112$), mercury ($Hg = 200$), calcium ($Ca = 40$), strontium ($Sr = 88$), barium ($Ba = 137$), platinum ($Pt = 98{\cdot}5$), and perhaps others. The elements of this class combine either two or more together and in very various proportions, *e. g.* ZnO, ZnS, SO^2, SO^3, CaS^5, Ba^2SO, $BaSO^2$, $BaSO^3$, $BaSO^4$, BaS^2O^3, BaS^2O^6, BaS^4O^6. They combine with the monatomic elements in the proportion of one atom or volume to two, forming compounds of which one molecule occupies twice the volume of the diatomic atom it contains, and the same volume as the two monatomic atoms: *e. g.* H^2O, Cl^2O, ClHO, KHS, &c. When more than one atom of a diatomic element enters into combination with one or more monatomic elements, the ratio of combination is sometimes much more complex: *e. g.* H^2O^2, Cl^2S^2, Cl^2SO, Cl^2SO^2, $KHSO^3$, $KHSO^4$, &c.‡

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* Fluorine is usually regarded as also belonging to this class, being associated with chlorine, bromine, and iodine; its known analogies to these bodies are not, however, either close or numerous, while its great tendency to unite at the same time with two different metals, or with hydrogen and a metal, seems to indicate that it ought rather to be placed in the next class of elements ($F = 38$, hydrofluoric acid $= FH^2$).

† This is not the only case in which iodine forms a compound of greater complexity than other members of the same class: for instance, iodic acid forms anhydro-salts, which are without analogues among the compounds of the other monatomic elements.

‡ Several elements are here enumerated as diatomic which are usually counted monatomic, and which are taken as such in the body of this work, on account of the inconvenience which would arise from the too great departure from established usage; partly also because the reasons for supposing some of them to be diatomic, though strong, cannot be considered quite conclusive. The question whether magnesium, zinc, cadmium, and mercury, and calcium, strontium, and barium, ought to be considered diatomic instead of monatomic, resolves itself into the question whether the accepted atomic weights of these elements ought to be doubled. We cannot discuss this question fully here, and must confine our-

2. *Triatomic Elements.*—Nitrogen ($N = 14$), phosphorus ($P = 31$), arsenic ($As = 75$), antimony ($Sb = 121$), bismuth ($Bi = 208$); boron ($B = 11$); gold ($Au = 197$); probably molybdenum ($Mo = 48$), vanadium ($Vd = 68 \cdot 5$), tungsten ($W = 92$); and perhaps others.

These elements do not form many combinations among themselves not containing any element belonging to another class. They combine with the monatomic elements in the proportion of 1 at. to 3, to form such bodies as NH^3, PH^3, AsH^3, $SbAg^3$, $BiCl^3$, BCl^3, $AuCl^3$, &c.; 1 at. of some of them can also combine with 5 monatomic atoms, many bodies of the following form being known: NH^4Cl, PH^4I, PCl^5, &c.; but none of these compounds appear to be capable of volatilising without decomposing, so as to regenerate a compound of the class first mentioned, as shown in the following examples:—

$$NH^4Cl = NH^3 + HCl$$
$$PCl^5 = PCl^3 + ClCl.$$

With the diatomic elements and with the diatomic and monatomic elements together, they combine in very various proportions, but always so that the sum of the triatomic atoms, or of the triatomic and monatomic atoms together, when the latter are present, contained in a molecule of the products formed, is an even number.

3. *Tetratomic Elements.*—Carbon ($C = 12$), silicon ($Si = 28 \cdot 5$), titanium ($Ti = 48 \cdot 5$), tin ($Sn = 118$), tantalum ($Ta = 138$); probably lead ($Pb = 207$), and perhaps other elements.

These elements can combine with the monatomic elements in the proportion of 1 at. to 2 (*e. g.* $SiCl^2$, $SnCl^2$), and with the diatomic elements in the proportion of 1 at. to 1 (*e. g.* CO, SiO, SnO); but the compounds so produced readily combine with 2 monatomic atoms, or with 1 diatomic atom, to form such bodies as the following: $SiCl^4$, $SnCl^4$, $COCl^2$, CO^2, SiO^2, &c., which appear to represent the normal compounds of the tetratomic elements. They also form very many compounds with the triatomic elements, or with these and the monatomic or diatomic elements together. The following are examples of the simplest combinations so produced:

$$C^2N^2,\ CNH,\ CNHO.$$

4. *Hexatomic Elements.*—The following elements are perhaps hexatomic: iron ($Fe = 112$), aluminium ($Al = 54$), and other similar bodies.

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selves to the statement of certain facts whose bearing on the point will be understood if the reader has studied the article ATOMIC WEIGHTS.

α. *Magnesium, Zinc, Cadmium, Mercury.*—Of these four elements it may be said, that the evidence in favour of doubling the atomic weights of zinc and mercury is conclusive, while magnesium and cadmium are so obviously members of the same natural family, that it is not possible to double the atomic weights of the former two metals without doubling theirs also. The most important reason for doubling the atomic weights of zinc and mercury are the following:—When these metals act upon the iodides of the alcohol-radicles, 65 pts. zinc or 200 pts. mercury combine directly with the quantities represented by the formulæ CH^3I, C^2H^5I, $C^5H^{11}I$, C^3H^5I, in each case forming a single product, such as $Zn''C^2H^5I$, $Hg''C^2H^5I$, $Hg''C^3H^5I$, &c., as though 65 pts. zinc and 200 pts. mercury, represented indivisible quantities, or atoms, of those metals, whereas if these weights represented two atoms, we should expect that the action of 65 pts. zinc or of 200 pts. mercury on C^2H^5I would give rise to two distinct products, ethylide and iodide of zinc or of mercury. The combination which actually takes place is analogous to the combination of (the diatomic element) oxygen with cyanide of potassium:

$$KCy + O = KCyO\,;$$

if zinc and mercury were monatomic, their action on the hydriodic ethers would probably be analogous to that of (the monatomic element) chlorine on cyanide of potassium:

$$KCy + Cl^2 = KCl + CyCl.$$

Again, the reactions represented by the following equations (and the similar reactions which take place with mercury-methyl) all tend to show that a molecule of mercury-ethyl (or mercury-methyl) contains 2 at. ethyl (or methyl):

$$\overset{''}{Hg}(C^2H^5)(C^2H^5) + BrBr = \overset{''}{Hg}(C^2H^5)Br + C^2H^5.Br \text{ (Buckton).}$$
$$\overset{''}{Hg}(C^2H^5)(C^2H^5) + ClH = \overset{''}{Hg}(C^2H^5)Cl + C^2H^5.H \text{ (Buckton).}$$
$$\overset{''}{Hg}(C^2H^5)(C^2H^5) + \overset{''}{Hg}ClCl = \overset{''}{Hg}(C^2H^5)Cl + \overset{''}{Hg}Cl(C^2H^5) \text{ (Buckton),}$$

and it is difficult to understand what can cause the two atoms of alcohol-radicle to remain combined, if it be not that the quantity of mercury with which they are united is one indivisible atom.

To these chemical arguments may be added that drawn from the determinations which have been made of the vapour-densities of zinc and mercury compounds. All the determinations hitherto made agree with the supposition that the atomic weights of these metals are 65 and 200 respectively, and not 32·5 and 100, as generally admitted; the specific heats of these metals point also to the same conclusion.

We may add, finally, that the readiness with which all the four metals under consideration form basic salts is a further indication of their diatomic character.

β. *Calcium, Strontium, Barium.*—The decomposition of the hydrates of these metals by heat alone, taken in connection with their general close resemblance to the alkalis, may be regarded as evidence of their being hydrates of diatomic radicles bearing the same relation to the hydrates of potassium, sodium, &c., that the bibasic acids (most of which are similarly decomposed by heat) bear to the monobasic acids. Moreover, the non-existence of acid carbonates, sulphates, oxalates, &c., of any of them seems to show that the quantities of metal (twice the quantities usually admitted as representing their atomic weights) contained in their neutral salts with bibasic acids are indivisible. Notwithstanding, however, these and some other indications of a diatomic character, the atomicity of calcium, strontium, and barium must be considered as still more or less open to question.

The existence of this class is not as yet certainly proved; there is, however, reason to believe that iron, aluminium, and perhaps some of the metals most closely allied to them, are hexatomic, and that their simplest compounds with the monatomic elements contain 6 monatomic atoms (*e.g.* sesquichloride of iron, $FeCl^6$; chloride of aluminium, $AlCl^6$).

Notwithstanding the exceptions which we have pointed out, the difference in the modes of combination of various elements, which have been indicated as serving for their division into distinct classes, are in the main so marked and so constant as almost to make the conclusion unavoidable that they result from differences in the combining capacity of the elementary atoms themselves; that in fact the *atomic combining capacity* or *atomicity* of the various elements is a definite and fixed property comparable to their atomic weight. And, if it be accordingly admitted that an atom of oxygen, or of any other element of the same class, can combine with *twice* as great a weight of any given element as an atom of hydrogen, or of any other element of its class,—that an atom of any element of the nitrogen-class can combine with *three* times as much, and an atom of any element of the carbon-class with *four* times as much (that is, if the terms monatomic, diatomic, triatomic, and tetratomic, applied to the various classes into which the elementary bodies have been divided, be admitted to correspond to actual differences in the combining powers of the *atoms* of the elements),—then it is possible to explain, at least to a very great extent, the general differences of composition which the compounds of these elements show when compared together.

Upon the classification of the elementary bodies which we have here adopted, we have now to found a classification of their compounds. [In this part of the subject it will often be convenient to use the following general signs for denoting elements of the various classes:

For monatomic elements, a vertical or horizontal stroke: | or —

For diatomic elements, two such strokes connected at one end by a straight line  or 

For triatomic elements, three strokes connected:  or 

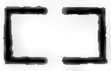
For tetratomic elements, four strokes connected:  or 

The number of strokes in the sign of each class of elements thus represents their atomicity.]

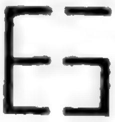
The simplest normal combinations which one monatomic, diatomic, triatomic, or tetratomic atom respectively can form, are the following:

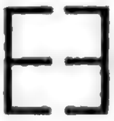
1. Monatomic atom with monatomic, — —; example: $\overset{\prime}{H}\overset{\prime}{Cl}$.

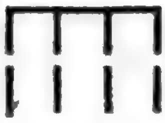
2. *a.* Diatomic atom with 2 monatomic, ; examples: $\overset{\prime\prime}{O}\overset{\prime}{H}{}^2$, $\overset{\prime\prime}{O}\overset{\prime}{H}\overset{\prime}{K}$.

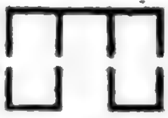
b. Diatomic atom with diatomic, ; example: $\overset{\prime\prime}{O}\overset{\prime\prime}{Hg}$.

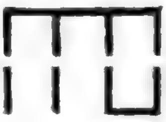
3. *a.* Triatomic atom with 3 monatomic, ; example: $\overset{\prime\prime\prime}{N}\overset{\prime}{H}{}^3$, $\overset{\prime\prime\prime}{N}\overset{\prime}{H}{}^2\overset{\prime}{K}$.

b. Triatomic atom with 1 monatomic and 1 diatomic, ; examples: $\overset{\prime\prime\prime}{N}\overset{\prime}{Cl}\overset{\prime\prime}{O}$ $\overset{\prime\prime\prime}{Sb}\overset{\prime}{Cl}\overset{\prime\prime}{O}$.

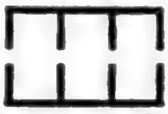
c. Triatomic atom with triatomic, ; example: $\overset{\prime\prime\prime}{N}\overset{\prime\prime\prime}{B}$.

4. *a.* Tetratomic atom with 4 monatomic, ; examples: $\overset{iv}{C}\overset{\prime}{H}{}^4$, $\overset{iv}{C}\overset{\prime}{H}\overset{\prime}{Cl}{}^3$, $\overset{iv}{C}\overset{\prime}{H}{}^2\overset{\prime}{I}{}^2$.

b. Tetratomic atom with 2 diatomic, ; examples: $\overset{iv}{C}\overset{\prime\prime}{S}{}^2$, $\overset{iv}{Si}\overset{\prime\prime}{O}{}^2$.

c. Tetratomic atom with 2 monatomic and 1 diatomic, ; examples: $\overset{iv}{C}\overset{\prime}{Cl}{}^2\overset{\prime\prime}{O}$, $\overset{iv}{Pb}\overset{\prime}{Cl}{}^2\overset{\prime\prime}{O}$.

d. Tetratomic atom with 1 monatomic and 1 triatomic, ; example: $\overset{iv}{C}H\overset{'''}{N}$.

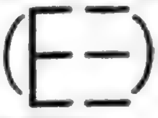
e. Tetratomic atom with tetratomic, 

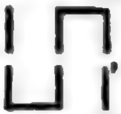
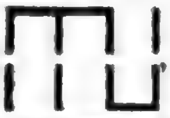
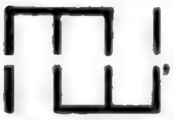
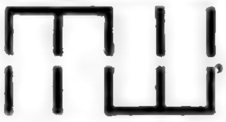
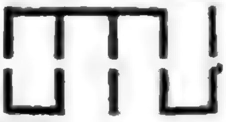
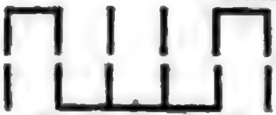
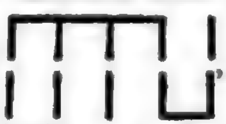
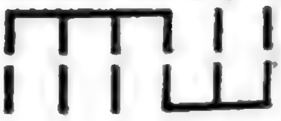
It will be seen that this classification of compounds of the simplest order is equivalent to Gerhardt's classification according to types. Compounds of the form 1 are those referred by him to the type HCl or HH; those of the form 2*a*, are those referred to the type H^2O; those of the form 3*a*, are those referred to the type H^3N; while bodies of the form 4*a* may be referred to the type H^4C, subsequently introduced (by Odling, Kekulé, and others) for the purpose of further extending Gerhardt's system. The sub-forms 2*b*, 3*b*, 3*c*, 4*b*, 4*c*, 4*d*, 4*e*, may be regarded as deriving from the primary forms, if we take account of the multequivalency of the polyatomic elements (see EQUIVALENTS), and consider, for instance, chloroxide of carbon (4*c*) as representing a body of the form 4*a*, in which the diequivalent atom O takes the place of 2 monatomic atoms, and hydrocyanic acid (4*d*) as a body of the same form in which the triequivalent atom N takes the place of 3 monatomic atoms. In this way all bodies such as those above mentioned, may be referred to the four types HCl, H^2O, H^3N, H^4C; so far, then, the empirical classification of Gerhardt, and that which we have here deduced from the theoretical basis of the definite atomicity of the elements, are identical.

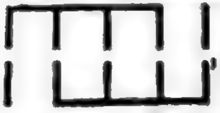
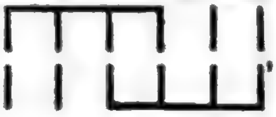
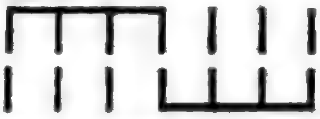
In order to extend his classification to compounds of a higher degree of complexity, Gerhardt was obliged to assume the existence of an indefinite number of compound radicles: we have now to consider the constitution of such compounds, and shall thus see that the idea of the atomicity of the elements includes, not only the idea of types, but also the idea of compound radicles,—ideas which recent chemistry has shown to be correlative, neither of them having any significance except in relation to the other.

Comparing now more complex compounds with each other and with the very simple compounds of which we have been speaking, we find that, whereas there is no rule as to the number of diatomic or tetratomic atoms which one compound may contain more or less than are contained in another, the difference between the number of monatomic or of triatomic atoms, or of monatomic and triatomic atoms together when both are present, contained in two well defined and well analysed bodies, is always an even number. But since the compounds constituted according to any of the forms above enumerated always contain an even number of monatomic, or of triatomic, or of monatomic and triatomic atoms together, this amounts to saying that *the sum of such atoms contained in any well-defined and well-analysed body is always an even number.* This proposition embodies one of the earliest observed regularities in the atomic composition of compound bodies (*vid.* Laurent, Ann. Ch. Phys. [3] xviii. 266), often spoken of as *the law of the even number of atoms*, and is in strict accordance with the view which regards the combination of the elements as consisting in the mutual saturation of their atomic combining capacities, and might indeed be deduced from it; for since each unit of combining capacity requires another for its saturation, the number of atoms in every normal compound (or compound in which the atomicity of each element is saturated) must be such that the number representing the sum of their combining capacities is even; and this can only be the case when it contains an even number of those atoms (monatomic and triatomic atoms) whose atomicity is represented by an odd number.

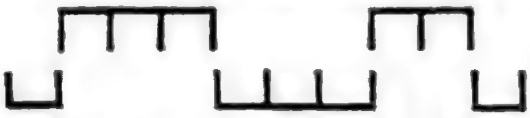
The highest number of monatomic atoms that any compound can contain appears to be regulated by the number and nature of the polyatomic atoms which it contains. If a compound contain n polyatomic atoms whose atomicities are respectively A, A′, A″, &c., the highest number of monatomic atoms that it can contain is $A + A' + A'' + \ldots . - 2(n-1)$; but it may contain any lower number differing from this by a multiple of 2.

We may illustrate this rule by applying it to the simplest normal compounds of atoms of each degree of atomicity. In the case of compounds of the form 1 (– –), A + A′, &c., = 0, n also = 0, therefore the formula becomes $-2(-1) = 2$; in the case of compounds of the form 2*a*, (), A′, A″, &c., disappear, and $n = 1$, so that the term $2(n-1)$ also disappears, and the formula is reduced to $A = 2$, in like manner in the case of compounds of the form 3*a*, (), the formula becomes $A = 3$; and in the case of those of the form 4*a*, (), it becomes $A = 4$. All compounds belonging to any of these four classes, contain therefore the maximum number of monatomic atoms. We have previously alluded to some substances in which this maximum appears to be exceeded: namely, first, compounds containing *four* or *six* monatomic atoms, such as $NaAgCl^2$ (?) and K^2AgI^3; secondly, compounds containing *five* monatomic atoms to one triatomic atom, such as NH^4Cl, PCl^5, &c. There is, however, as already pointed out, reason to believe that all such bodies as these are not strictly speaking chemical individuals, but that they are combinations of entire molecules, as such, held together by a force analogous to that which causes certain salts to combine with water of crystallisation. This view may be easily admitted with reference to the first set of exceptional substances, because they cannot be proved to exist, except in the crystalline state: being generally decomposed by solution in a moderate quantity of water, they are often not very constant in the proportions of their ingredients, and the two salts, of which they may be regarded as made up, retain their usual properties without essential alteration. In the case of some of the second class of exceptional bodies, the difficulties in the way of admitting this explanation are greater. These bodies are so numerous, and some of them form so readily and are under certain ordinary conditions so stable, that some chemists have been led to regard nitrogen, phosphorus, arsenic and antimony as pentatomic instead of triatomic. The chief reason for not adopting this conclusion is that, in all such compounds, two of the monatomic atoms appear to be more loosely combined than the other three, so that even the most stable compounds of this kind, namely the ammonia-salts, are always decomposed to a greater or less extent by the evaporation of their solutions, and not one body of this class appears to be volatile without decomposition (into a compound of the form 1, and a compound of the form 3*a*). But whatever be the real nature of these compounds and of the force which causes their formation, it is certain that they differ in important respects from substances whose composition accords with the atomicity of their components, and that their properties are to a great extent explicable if we regard them as combinations of entire molecules produced independently of the combining capacities of their constituent atoms. (To prevent repetition, we may state here that the same view is applicable to all other compounds of ammonia and similar bodies with acids.)

But to return and consider how far the composition of other bodies agrees with the formula which we have said gives the highest possible number of monatomic atoms that they can contain. It results from the formula that bodies containing two diatomic atoms can contain also two monatomic atoms. Accordingly there exist not only compounds of the form  (referred to above by the number 2*b*), but also compounds of the form , for example, $SOCl^2$, O^2H^2. For bodies containing one triatomic and one diatomic atom, the formula gives 3 as the highest number of monatomic atoms that they can contain; accordingly, in addition to compounds of the form 3*b*, there exist compounds of the form , for example, $NOCl^3$, $POCl^3$. Bodies like those of the form 3*c*, containing two triatomic atoms may, according to the formula, contain at most four monatomic atoms: agreeably with this result, compounds are known of the form , for example, $NPCl^2$, and of the form , for example, P^2I^4. Bodies containing one tetratomic and two diatomic atoms (4*b*) may by the same rule contain *four* monatomic atoms: hence we may have bodies of the form  example, CO^2H^2 (formic acid), and bodies of the form ; methylic glycol, CO^2H^4, if known, would be an example of this class. Similarly, bodies containing one tetratomic and one diatomic atom (4*c*) may contain four monatomic atoms, forming compounds of the form , for example, COH^4 (methylic alcohol), CSH^4 (methylic mercaptan); bodies containing one tetratomic and one triatomic atom (4*d*) may contain five monatomic atoms, forming compounds of the form 

for example, CNH^5 (methylamine); and bodies containing two tetratomic atoms (4*e*), may contain two, four, or six monatomic atoms giving compounds of the form , example, C^2H^2 (acetylene); , example, C^2H^4 (ethylene); or  example, C^2H^6 (hydride of ethyl)

The question now arises, how far is this law of the combination of the different elements in accordance with the idea of their having each a definite and constant atomicity? A little consideration will show that it is a necessary consequence of that supposition. The total combining capacity of any number of atoms is evidently the sum of their several combining capacities, and if these latter be denoted by A, A', A'', &c., will be expressed by $A + A' + A'' + \ldots.$; but if the atoms be combined together, their total combining capacity will not be so great as in the free state, it will have been more or less saturated by the combination which has taken place among them. The atomicity of as many of them as are monatomic, will have been entirely saturated by the combination, but the atomicity of such as are polyatomic may be only partially saturated; and it will be saturated to the smallest possible extent if, of all but two of them, two units of combining capacity be saturated each by one unit of a different atom, and if one unit of each of the remaining two atoms be saturated. This mode of combination is shown by the following diagram, representing 2 tetratomic atoms, 1 triatomic atom, and 2 diatomic atoms combined in the way described: —



Since the free atomicity (if we may use the expression) of all but two atoms is thus diminished by two units, and the free atomicity of each of the remaining two atoms is diminished by one unit, the total remaining free atomicity of the group is equal to the total atomicity of the uncombined atoms (or $A + A' + A'' + \ldots.$), diminished by $(2(n-2) + 2)$,

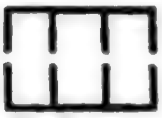
$$\text{that is:}\quad A + A' + A'' + \ldots. -2(n-2) - 2 = A + A' + A'' + \ldots. -2(n-1),$$

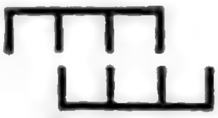
which is the precise expression, some of whose consequences we have above discussed.

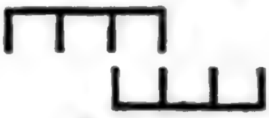
It is evident that no combination can take place without the saturation of at least two units of atomicity, one belonging to each of the combining atoms. Hence, when a monatomic atom combines with any other atom, or group of atoms, the atomicity of the product must be one less than that of such atom or group of atoms: for the monatomic atom brings to the compound that is formed only one unit of atomicity, whereas two units are saturated by the combination. Therefore, as we have seen, the number of monatomic atoms with which any atom or group of atoms can combine, is always limited. For similar reasons the total atomicity of any atom or group is the same as that of its compound with a diatomic atom. From this follow the several consequences: first, there is *a priori* no assignable limit to the number of diatomic atoms with which a given atom or group may combine; secondly, compounds which do not contain atoms whose atomicity is represented by a higher number than 2, never contain more than two monatomic atoms; *e.g.* water, H^2O, and sulphydric acid, H^2S, each contain two monatomic and one diatomic atom, while pentathionic acid, $H^2S^5O^6$, contains eleven diatomic, but still only two monatomic atoms; thirdly, compounds containing the maximum number of monatomic atoms do not become able to combine with a greater number through union with any number of diatomic atoms; *e.g.* hydride of hexylene, C^6H^{14}, contains the maximum of monatomic atoms, but mannite, $C^6H^{14}O^6$, differing from it by containing O^6 additional, is not capable of further combination with monatomic atoms. When a triatomic atom enters into combination, it brings to the compound three units of atomicity, and two units are saturated by the combination, so that the entire atomicity of the product exceeds that of the original substance by one. Hence, when a triatomic element, as nitrogen, combines with a group already containing the maximum of monatomic atoms, the group becomes able to take up an additional monatomic atom; accordingly, we have many compounds which differ by NH, or a multiple of it, *e.g.*, C^2H^6 (hydride of ethyl), C^2H^7N (ethylamine), $C^2H^8N^2$ (ethylene-diamine); C^2H^4O (aldehyde), C^2H^5NO (acetamide); $C^2H^4O^2$ (acetic acid), $C^2H^5NO^2$ (glycocine). When a tetratomic atom is added to a group, the total atomicity of the product in like manner exceeds that of the original substance by 2. Hence the possibility of the many series of compounds of which the terms differ by CH^2 or by a multiple thereof.

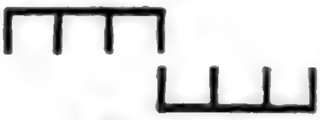
It will be understood that the foregoing remarks touching the combining capacity of various atomic groupings, and the way in which it is affected by the addition of atoms of various kinds, have reference only to the *highest number* of monatomic atoms that is ever found in combination with a given number of polyatomic atoms; and that it is by no means intended to imply that all compounds contain, or even show any great tendency to combine with, the whole number of monatomic atoms which the rules above given indicate as the maximum in each case. Several compounds not containing the maximum of monatomic atoms have already been incidentally referred to; but it is necessary that the constitution of such compounds should be somewhat more specially discussed in relation to the theory of the definite combining capacity of the elementary atoms.

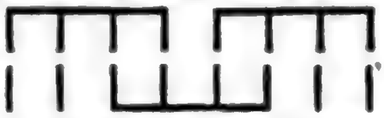
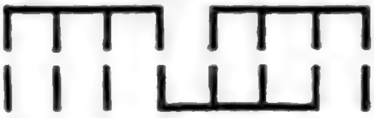
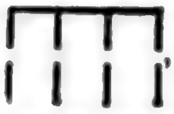
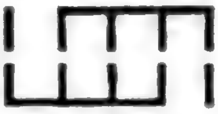
According to this theory, there are four different ways in which it is possible for two tetratomic atoms, for instance, two atoms of carbon, to combine. Two such atoms may mutually saturate, either the whole, three fourths, one half, or one fourth of each other's combining capacity, as expressed by the following diagrams: —


Each atom completely saturated.


Each atom ¾ saturated.


Each atom ½ saturated.


Each atom ¼ saturated.

The first diagram probably represents some variety of free carbon; the second, third, and fourth, the manner in which the two carbon-atoms are combined in acetylene, C^2H^2, ethylene, C^2H^4, and hydride of ethyl, C^2H^6, respectively. In the last of these bodies, one unit only of the combining capacity of each carbon-atom is saturated by the other, leaving three units of affinity belonging to each free for combination with hydrogen; and it is plain that two atoms of carbon can only combine with a larger number of hydrogen, or other monatomic atoms, than are contained in this compound, when they are entirely uncombined with each other. In ethylene and acetylene, on the other hand, the two atoms of carbon are so combined that, if we may so speak, they can combine with an additional number of monatomic atoms by loosening, without entirely giving up, their hold upon each other. And in all compounds in which the proportion of monatomic to polyatomic atoms is below the maximum indicated by the formula given higher up, we must, unless we suppose the atomicity of the elements to be variable (in which case the word atomicity ceases to have any special meaning), suppose that a greater or lesser number of the polyatomic atoms are combined in a similar way. But, in the great majority of such cases, the composition alone of a compound does not enable us to decide as to how many of its polyatomic atoms are in this kind of more intimate union with each other. For example, allylene, C^3H^4, homologous with acetylene, might, so far as its mere composition is concerned, be constituted either thus , or thus ; its properties, however, would be somewhat different in the two cases. It would not be possible to combine a compound constituted in the first manner with two atoms of hydrogen, without transforming it into propylene, C^3H^6, or an isomeric body; but it would doubtless be possible, under appropriate conditions, to cause a body constituted in the second manner to split up, by the addition of two atoms of hydrogen, into marsh-gas, CH^4 or , and acetylene, C^2H^2, or .

In the preceding part of this article, we have tried to show that those of the elements which have been sufficiently studied may be divided into distinct classes, according to the manner in which they enter into combination, and further, that each element possesses a certain definite atomic combining capacity, which regulates the formation of its most complex as well as of its simplest compounds. By the application of this principle of the definite atomicity of the elements, it would be easy to construct tables showing all the possible combinations of each element; all compounds whose constitution was sufficiently understood, might then be classified by inserting them in their places in these tables. But since the place of any compound would be determined, not only by its composition, but also by the mode or order of combination of its atoms, a point concerning which we have, in most cases, no definite knowledge, such a system of classification would not be widely applicable in the present state of chemistry. Our acquaintance with the great majority of the more complex compounds consists in the knowledge of transformations, by which only a small number of their atoms are affected. It has, therefore, been found convenient, for the purposes of classification to regard such compounds as consisting of two parts, namely, the atom or atoms which take part in their known transformations, and a residue, or nucleus, or radicle, which is unaffected by these transformations, and appears as a constant constituent in all the products to which they give rise. By aid of this convention, the classification founded upon the atomicity of their elements, which, as we have seen, is applicable to the more simple compounds, may be extended so as to comprehend all tolerably well known substances. The radicles, whose existence this view supposes, may be of any degree of complexity; their nature and their relation to the compounds in which they are contained will be most easily understood by considering a few of the simplest of them.

Hydrochloric acid, HCl, water, H^2O, ammonia, H^3N, and marsh-gas, H^4C, have already been shown to be compounds, each of which may be taken as the representative of a whole class of bodies. If we imagine 1 atom of hydrogen to be removed from each of these substances, it is plain that the residues Cl, HO, H^2N, H^3C, will each be able to combine with an atom of hydrogen to reproduce the original compounds, or with some other monatomic atom, such as chlorine or potassium, to form such bodies as:

$$KCl,\ ClCl;\quad KHO,\ ClHO;\quad KH^2N;\quad KH^3C,\ ClH^3C;\ \&c.$$

It is plain also, since 1 at. of a diatomic element is equivalent in combining capacity to 2 monatomic atoms, that 1 at. of oxygen, sulphur, &c., will combine with 2 at. of each of these residues, or with two different residues at once, or with 1 at. of a residue and with 1 at. of a monatomic element, forming such compounds as the following:

$$O\left\{\begin{matrix}Cl\\Cl\end{matrix}\right.,\quad O\left\{\begin{matrix}H^3C\\H^3C\end{matrix}\right.,\quad O\left\{\begin{matrix}H^3C\\H^5C^{2}*\end{matrix}\right.,\quad O\left\{\begin{matrix}H^3C\\H\end{matrix}\right.,\quad O\left\{\begin{matrix}H^3C\\K\end{matrix}\right.,\ \&c.$$

For similar reasons, it is evident that 1 at. of a triatomic element will combine with 3 at. of such residues, or with 2 at. of residue and 1 at. of a monatomic element, or with 1 at. of residue and 2 monatomic elementary atoms, *e. g.*:

$$N\left\{\begin{matrix}Cl\\Cl\\Cl\end{matrix}\right.,\quad N\left\{\begin{matrix}H^3C\\H^3C\\H^3C\end{matrix}\right.,\quad N\left\{\begin{matrix}H^3C\\H^5C^2\\H^{11}C^5\dagger\end{matrix}\right.,\quad N\left\{\begin{matrix}H^3C\\H^3C\\H\end{matrix}\right.,\quad N\left\{\begin{matrix}H^3C\\H\\H\end{matrix}\right.,\ \&c.$$

In like manner, 1 at. of a tetratomic element will combine with 4 at. of residue, or with 4 at. partly of residue and partly elementary, *e. g.*:

$$C\left\{\begin{matrix}Cl\\Cl\\Cl\\Cl\end{matrix}\right.,\quad C\left\{\begin{matrix}H^3C\\H\\H\\H\end{matrix}\right.,\quad C\left\{\begin{matrix}HO\\H\\H\\H\end{matrix}\right.,\quad C\left\{\begin{matrix}HO\\H^3C\\H\\H\end{matrix}\right.,\ \&c.$$

From all this it follows that these residues or radicles follow the same laws of combination with the elementary bodies of different classes as do the monatomic elements themselves. Further, they combine also with one another according to the same laws as are followed by elementary monatomic atoms; that is, they combine together in the proportion of 1 at. to 1 at., *e. g.*:

$$Cl + H^3C = ClH^3C$$

Chloride of methyl.

$$HO + H^3C = OH^3C$$

Methylic alcohol.

$$H^2N + H^3C = NH^5C$$

Methylamine.

$$H^3C + H^3C = H^6C^2$$

Free methyl.

But, just as there are not only monatomic but also polyatomic elements, so there are polyatomic as well as monatomic radicles. If we suppose H^2 to be withdrawn from each of the compounds H^2O, H^3N, H^4C, it is evident that the residues O, HN, H^2C, will have the properties of diatomic radicles, the compound radicles HN and H^2C being similar in their combining capacity to the simple radicle O, just as the compound radicles HO, H^2N, and H^3C, resemble the simple radicle Cl in their combining capacity. After the detailed illustration of the properties of the monatomic radicles given above, it is not necessary to dwell upon the characters of the diatomic radicles, since what has been said of the former applies, *mutatis mutandis*, to the latter.

In like manner, the abstraction of H^3 from H^3N and H^4C gives the triatomic radicles N and HC; and the withdrawal of H^4 from any normal compound leaves a tetratomic radicle analogous in properties to the simple radicle C, which results from the withdrawal of H^4 from H^4C.

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* $H^5C^2 = H^6C^2 - H$: it is a residue or radicle comparable to H^3C.

† $H^{11}C^5 = H^{12}C^5 - H$.

Although, in considering the properties and combinations of these or of other compound radicles, we may confine our view to their analogies with the elementary bodies and regard their atomicity as an ultimate property, which, like the atomicity of the elements, is not to be explained, it is easy to see that the atomicity of the radicles of which we have spoken, is the direct result of their composition and the atomicity of their component atoms. It only requires to be put into words to be at once evident that, if one, two, three, or more monatomic atoms be removed from any normal compound whatever, the remainder will be a substance possessing one, two, three, or more units of atomicity free for combining with other bodies, and therefore, as to its power of combination, exactly analogous to an atom of an element whose atomicity is represented by one, two, three, or a higher number. Hence the derivation of any compound radicle determines its atomicity. The maximum atomicity of a radicle may also be always deduced from its composition by means of the formula $A + A' + A'' + \ldots - 2(n-1)$, in which A, A', A'', &c., indicate the atomicities of the elementary atoms, monatomic as well as polyatomic, of which the radicle is composed, and *n* the number of atoms it contains. From this formula it follows that a compound radicle can never consist of monatomic atoms only; that radicles containing only diatomic atoms are always diatomic; and that the atomicity of radicles containing only tetratomic, or tetratomic and diatomic atoms, is always represented by 2, 4, or some other even number. It follows also from the same formula, and from what has been previously said as to the composition of complex compounds in general, that, starting from the simple radicles already described, there may exist series of radicles of the same atomicity in which the common difference is , *e. g.* O; or , *e.g.* HN; or , *e.g.* CH^2.

For example:

Common difference, 		*Common difference,* 		*Common difference,* 		
Cl	O	HO	H	CH^3	CH^2	CH
ClO	SO	PH^2O (in hypophosphites)	NH^2	C^2H^5	C^2H^4	C^2H^3
ClO^2	SO^2			C^3H^7	C^3H^6	C^3H^5
ClO^3				&c.	&c.	&c.
ClO^4						

From these, considered as primary radicles, so-called *derived* or *conjugate* radicles may arise by equivalent substitution; for instance, by substitution of Cl, Br, or I, for H; of O or S for H^2; of S for O; of N for H^3, or for HO^3, &c.; or of NO^2 or NH^2 for H; or of SO^2 or CO for H^2, or generally of any radicle for its equivalent. Again, still other radicles exist differing from these by containing some multiple of H^2 (or its equivalent) less than they do, but possessing the same atomicity; for example, we have ethyl, C^2H^5, and vinyl, C^2H^3; trityl, C^3H^7, and allyl, C^3H^5; propionyl, C^3H^5O, and acryl, C^3H^3O; hexyl, C^6H^{13}, and phenyl, C^6H^5; all of them monatomic radicles.

Hence it follows that triatomic radicles may often be isomeric with monatomic radicles; for example, *acetyl* (Berzelius) C^2H^3, triatomic, with *vinyl*, C^2H^3, monatomic; *glyceryl*, C^3H^5, triatomic, with *allyl*, C^3H^5, monatomic; in like manner, tetratomic and diatomic radicles may be isomeric with each other; for example, *tartryl*, $C^4H^2O^2$, tetratomic (tartaric acid = $\left.\begin{matrix}(C^4H^2O^2)^{iv}\\ H^4\end{matrix}\right\}O^4$), with *fumaryl*, $C^4H^2O^2$, diatomic (fumaric acid = $\left.\begin{matrix}(C^4H^2O^2)''\\ H^2\end{matrix}\right\}O^2$). In such cases, we must suppose that the carbon (or other polyatomic atoms) of the radicles which contain a smaller proportion of hydrogen, or which have a lower atomicity, are more intimately combined with each other than they are in those which, having the same atomicity, contain a larger proportion of hydrogen, or with the same composition have a higher atomicity.

We have hitherto spoken only of the composition and atomicity of compound radicles; it remains to explain a little more fully the grounds upon which their existence in various compounds is assumed, and what that assumption is intended to imply. It has been said that compound radicles are groups of elements which are contained in a greater or lesser number of bodies, and are unaltered in the reactions by which one of these is transformed into another. For instance, the bodies of the following series:—

C^7H^6O	Oil of bitter-almonds,
C^7H^5ClO	Chloride of benzoyl,
$C^7H^6O^2$	Benzoic acid,
C^7H^7ON	Benzamide,
C^8H^5ON	Cyanide of benzoyl,

contain the group C^7H^5O (benzoyl) as a common constituent which remains unchanged when they are transformed one into another. Now the reactions by which these transformations are effected are essentially quite similar to those by which the following bodies are changed one into another.—

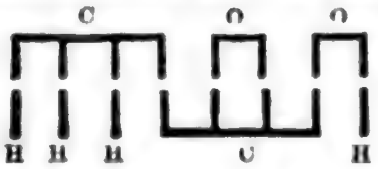
KH (?)	Hydride of potassium.
KCl	Chloride of potassium.
KHO	Hydrate of potassium.
KH^2N	Potassamine.
KCN	Cyanide of potassium.

This analogy is hidden if the formulæ of the bodies of the former series are written as above; but if they are written as containing the compound radicle benzoyl, C^7H^5O, the analogy becomes at once apparent:

$(C^7H^5O)H$	Hydride of benzoyl, or oil of bitter-almonds.
$(C^7H^5O)Cl$	Chloride of benzoyl.
$(C^7H^5O)HO$	Hydrate of benzoyl, or benzoic acid.
$(C^7H^5O)H^2N$	Benzamide.
$(C^7H^5O)CN$	Cyanide of benzoyl.

These latter formulæ express that the bodies represented by them are functionally analogous to compounds of the monatomic elements, and that they respectively possess the general properties of those classes of bodies of which HCl, H^2O, H^3N, &c., are the typical representatives.

The precise nature of the radicle which any substance is represented as containing will naturally vary according as it is desired to express the relations of the substance in question to this or that series of other bodies, or its capability of undergoing this or that series of transformations. If, for example, we wish to express the relation in which acetic acid stands to aldehyde, chloride of acetyl, acetamide, &c., we shall do so most simply by representing it as the hydrate of the compound radicle acetyl, C^2H^3O, thus, $\left.\begin{matrix}C^2H^3O\\H\end{matrix}\right\}O$. But if it be desired to express also that, by distillation with excess of alkali, by electrolysis, or by distillation with arsenious acid, acetic acid is resolved into a compound of the methyl series and a compound of the carbonic series, and that it can be formed from sodium-methyl and carbonic anhydride, or from cyanide of methyl by the action of alkali, this must be expressed by representing the radicle C^2H^3O as composed of the simpler radicles CH^3 and CO; and if we further wish to express the analogy of acetic acid to formic acid, we must write acetyl thus, $C(CH^3)O$, or as formyl, CHO, in which hydrogen is replaced by methyl: the whole formula of acetic acid then becomes $\left.\begin{matrix}C(CH^3)O\\H\end{matrix}\right\}O$. Similarly, in order to express the relations of acetic acid to still other sets of compounds, we are obliged to represent it as containing radicles of continually simpler composition, until finally we come to represent it as built up from elementary atoms; for instance, thus:



Hence the idea of a compound radicle is seen to be entirely relative, the same body from one point of view appearing to contain one compound radicle, and from another point of view appearing to contain a different one. A comparison of the definition of an elementary body, given near the begining of this article, with that of a componud radicle, shows that compound radicles bear the same relation to certain more or less limited sets of chemical processes that the elements bear to all the chemical processes known.

The application of the principles which we have been discussing, to the classification of chemical compounds generally, is illustrated by the following table, which is a modification and extension of that given by Gerhardt (*Traité*, iv. 612, 613), and reproduced in *Graham's Elements of Chemistry* (2nd edit. ii. 528, 529). By referring to the detailed commentaries by which Gerhardt's table of classification is followed in the places referred to, the reader will be able to understand fully the meaning of this table without requiring further explanation in this place.

Classification

Compounds comparable to **Hydrochloric Acid,** HCl.				*Compounds comparable*	
Containing monatomic radicles (Chlorides, Hydrides, &c.)	Containing diatomic radicles (Dichlorides, Dihydrides, &c.)	Containing triatomic radicles (Trichlorides, Trihydrides, &c.)	Containing tetratomic radicles Tetrachlorides, Tetrahydrides, &c.)	Containing monatomic radicles (Oxides, &c.)	Containing diatomic radicles (Dioxides, &c.)
Basic chlorides, hydrides, cyanides, &c.				**Basic oxides, sulphides,**	
Haloïd salts.					
(chloride of potassium, KCl).	(chloride of mercury, $HgCl^2$).	(chloride of antimony, $SbCl^3$).	(chloride of tin, $SnCl^4$).	1. *Primary*, or *hydrates* (hydrate of potassium, KHO).	1. *Primary* (hydrate of calcium, CaH^2O^2).
Metallic hydrides (hydride of copper, *&c.*)				2. *Secondary*, or *anhydrides* (oxide of potassium, K^2O).	2. *Secondary* (soda-lime, Na^2CaO^2).
Metals proper and alloys.					
(potassium, KK.)	(silver-amalgam.)				
Alcoholic chlorides, hydrides, &c.				**Alcoholic oxides,**	
Halogen ethers.					
(chloride of ethyl, C^2H^5Cl).	(chloride of ethylene, $C^2H^4Cl^2$).	(trichlorhydrine, $C^3H^5Cl^3$)		1. *Primary* (common alcohol, $(C^2H^5)HO$).	1. *Primary* (glycol, $(C^2H^4)H^2O^2$).
Metallic compounds of alcohol-radicles.					
(potassium-ethyl, KC^2H^5).	(zinc-ethyl, $Zn(C^2H^5)^2$).	(bismethyl, $Bi(C^2H^5)^3$).	(plumbethyl, $Pb(C^2H^5)^4$).	2. *Secondary* (common ether, $(C^2H^5)^2O$).	2. *Secondary*.
				Intermediate oxides,	
				Monatomic oxysalts and ethers (chlorate of potassium, $(ClO^2)KO$; acetate of ethyl, $(C^2H^3O)(C^2H^5)O$).	Diatomic oxysalts and ethers (sulphate of potassium, $(SO^2)K^2O^2$; sulphate of ethyl, $(SO^2)(C^2H^5)^2O^2$)
Acid chlorides, hydrides, &c.				**Acid oxides,**	
Aci-chlorides.					
(chloride of acetyl, $(C^2H^3O)Cl$).	(chloride of succinyl, $(C^4H^4O^2)Cl^2$).	(chloride of phosphoryl, $(PO)Cl^3$).		1. *Primary* (acetic acid, $(C^2H^3O)HO$).	1. *Primary* (sulphuric acid, $(SO^2)H^2O^2$).
Aldehydes, acetones, &c.					
(acetic aldehyde, $(C^2H^3O)H$; acetone, $(C^2H^3O)(CH^3)$).				2. *Secondary* (acetic anhydride, $(C^2H^3O)^2O$).	2. *Secondary* (succinate of ethylene, $(C^4H^4O^2)(C^2H^4)O^2$).

ccording to *Types.*

Water, H^2O.		*Compounds comparable to* **Ammonia,** H^3N.			
Containing triatomic radicles (Trioxides, &c.)	Containing tetratomic radicles (Tetroxides, &c.)	Containing monatomic radicles (Amines and Amides).	Containing diatomic radicles (Diamines and Diamides).	Containing triatomic radicles (Triamines and Triamides).	Containing tetratomic radicles (Tetramines and Tetramides).
elenides, &c.		**Basic nitrides, phosphides, arsenides, &c.**			
. *Primary* (hydrate of bismuth, BiH^3O^3).	1. *Primary.*	1. *Primary* (amide of potassium, KH^2N).	1. *Primary* (zincamide, $\overset{\prime\prime}{Zn}H^4N^2$).	1. *Primary.*	1. *Primary.*
Secondary (oxide of bismuth, Bi^2O^3).	2. *Secondary.*	2. *Secondary.*	2. *Secondary.*	2. *Secondary.*	2. *Secondary.*
		3. *Tertiary* (nitride of potassium, K^3N).	3. *Tertiary* (nitride of zinc, Zn^3N^2).	3. *Tertiary.*	3. *Tertiary.*
ulphides, &c.		**Alcoholic nitrides, phosphides, &c.**			
. *Primary* (glycerin, $(C^3H^5)H^3O^3$).	1. *Primary.*	1. *Primary* (ethylamine, $(C^2H^5)H^2N$).	1. *Primary* (ethylenediamine, $(C^2H^4)H^4N^2$).	1. *Primary.*	1. *Primary.*
Secondary (oxide of glyceryl, $(C^3H^5)^2O^3$).	2. *Secondary.*	2. *Secondary* (diethylamine, $(C^2H^5)^2HN$).	2. *Secondary* (diethylenediamine, $(C^2H^4)^2H^2N^2$).	2. *Secondary.*	2. *Secondary.*
		3. *Tertiary* (triethylamine, $(C^2H^5)^3N$).	3. *Tertiary* (triethylenediamine, $(C^2H^4)^3N^2$).	3. *Tertiary.*	3. *Tertiary.*
ulphides, &c.		**Intermediate nitrides, phosphides, &c.**			
riatomic oxysalts and ethers (phosphate of bismuth, $(PO)BiO^3$; phosphate of ethyl, $PO)(C^2H^5)^3O^3$).	Tetratomic oxysalts and ethers (orthosilicates, orthosilicate of ethyl, $Si(C^2H^5)^4O^4$).	Monalkalamides (ethyl-acetamide, $(C^2H^5)(C^2H^3O)HN$; silver-acetamide, $Ag(C^2H^3O)HN$).	Dialkalamides, (oxanilide, $(C^2O^2)(C^6H^5)^2N^2$).	Trialkalamides (citranilide, $(C^6H^5O^4)(C^6H^5)^3H^3N^3$)	Tetralkalamides.
ulphides, &c.		**Acid nitrides, phosphides, &c.**			
Primary (phosphoric acid, $(PO)H^3O^3$).	1. *Primary* (tartaric acid, $(C^4H^2O^2)H^4O^4$).	1. *Primary* (acetamide, $(C^2H^3O)H^2N$).	1. *Primary* (oxamide, $(C^2O^2)H^4N^2$).	1. *Primary* (phosphotriamide, $(PO)H^6N^3$).	1. *Primary.*
Secondary (phosphoric anhydride, $(PO)^2O^5$).	2. *Secondary.*	2. *Secondary* (diacetamide, $(C^2H^3O)^2HN$).	2. *Secondary.*	2. *Secondary.*	2. *Secondary.*
		3. *Tertiary* (dibenzoyl-sulpho-phenylamide, $(C^7H^5O)^2(C^6H^5SO^2)N$).	3. *Tertiary.* (trisuccinamide, $(C^4H^4O^2)^3N^2$).	3. *Tertiary.*	3. *Tertiary.*

The groups into which chemical substances are here divided, may be considered as representing the principal varieties, but they are far from including all chemical compounds. By means of polyatomic radicles, molecules may be built up of much greater complexity than any shown in this table. There appears to be no assignable limit to the number of such compounds or to the degree of complexity which they may reach. Without discussing these bodies at length, we shall be able, by a few examples, to illustrate their nature and their relation to more simple substances. One of the most remarkable series of bodies of the kind to which we refer, are the polyethylenic alcohols of Lourenço and Wurtz. These chemists have shown that glycol, $(C^2H^4)H^2O^2$, is able to fix upon itself the elements of several molecules of oxide of ethylene, so as to give the following series of products:

$(C^2H^4)^2H^2O^3$	$(C^2H^4)^3H^2O^4$	$(C^2H^4)^4H^2O^5$	$(C^2H^4)^5H^2O^6$	$(C^2H^4)^6H^2O^7$
Diethylenic alcohol.	Triethylenic alcohol.	Tetrethylenic alcohol.	Pentethylenic alcohol.	Hexethylenic alcohol.

The principal transformations of glycol (monethylenic alcohol) itself are most conveniently expressed by representing it as containing the diatomic radicle ethylene, C^2H^4. With this radicle we must suppose the 2 at. of oxygen contained in glycol to be combined in such a manner that half the combining capacity of each is saturated by half the combining capacity of the radicle, the other half of the combining capacity of each atom of oxygen being saturated by an atom of hydrogen. This view of the constitution of glycol is expressed by the following formula, $\begin{array}{ll} \mathrm{H} & \\ & \}\mathrm{O} \\ (C^2H^4)'' & \\ & \}\mathrm{O} \\ \mathrm{H} & \end{array}$. Thus regarded, glycol may be compared to water by representing it as two molecules of water in which H^2 is replaced by $(C^2H^4)''$. The polyethylenic alcohols then become comparable to glycol if viewed as 3, 4, 5, &c., molecules of water in which respectively $(C^2H^4)^2$, $(C^2H^4)^3$, $(C^2H^4)^4$, &c., replaces an equivalent quantity of hydrogen. This comparison is expressed by the formulæ by which these compounds are represented above; but their relation to glycol becomes perhaps still more apparent if the same formulæ be written a little differently, so as to be directly comparable with that last given for glycol. Below are the formulæ of some of them so written, side by side with sulphur-compounds, which may be regarded as of analogous constitution.

$$\begin{array}{ll} \mathrm{H} & \\ & \}\mathrm{O} \\ (C^2H^4)'' & \\ & \}\mathrm{O} \\ \mathrm{H} & \end{array}$$

Glycol.

$$\begin{array}{ll} \mathrm{Cl} & \\ & \}\mathrm{O} \\ (S)'' & \\ & \}\mathrm{O} \\ \mathrm{Cl} & \end{array}$$

Chlorosulphuric acid.

$$\begin{array}{ll} \mathrm{H} & \\ & \}\mathrm{O} \\ (C^2H^4)'' & \\ & \}\mathrm{O} \\ (C^2H^4)'' & \\ & \}\mathrm{O} \\ \mathrm{H} & \end{array}$$

Diethylenic alcohol ($= C^4H^{10}O^3$).

$$\begin{array}{ll} \mathrm{K} & \\ & \}\mathrm{O} \\ (S)'' & \\ & \}\mathrm{O} \\ (S)'' & \\ & \}\mathrm{O} \\ \mathrm{K} & \end{array}$$

Hyposulphite of potassium ($= S^2K^2O^3$).

$$\begin{array}{ll} \mathrm{H} & \\ & \}\mathrm{O} \\ (C^2H^4)'' & \\ & \}\mathrm{O} \\ (C^2H^4)'' & \\ & \}\mathrm{O} \\ (C^2H^4)'' & \\ & \}\mathrm{O} \\ (C^2H^4)'' & \\ & \}\mathrm{O} \\ (C^2H^4)'' & \\ & \}\mathrm{O} \\ \mathrm{H} & \end{array}$$

Pentethylenic alcohol ($= C^{10}H^{22}O^6$).

$$\begin{array}{ll} \mathrm{K} & \\ & \}\mathrm{O} \\ (S)'' & \\ & \}\mathrm{O} \\ (S)'' & \\ & \}\mathrm{O} \\ (S)'' & \\ & \}\mathrm{O} \\ (S)'' & \\ & \}\mathrm{O} \\ (S)'' & \\ & \}\mathrm{O} \\ \mathrm{K} & \end{array}$$

Pentathionate of potassium ($= S^5K^2O^6$).

After these remarks, and what has been previously said about the combinations of polyatomic elements and radicles in general, the following table will be intelligible without further explanation. It gives a list (probably almost complete) of the known compounds containing two or more atoms of the same carbonated radicle, and a few examples of compounds containing radicles composed of other elements, such as sulphuryl (SO^2) and phosphoryl (PO). Many other examples of compounds of a similar nature might be found among mineral substances both natural and artificial, and there can be little doubt that the complex silicates and other minerals belong to this class of compounds. In the table, compounds of the same radicle are arranged on the same horizontal line; those referable to the same type are arranged in the same vertical column.

Classification according to Types (continued).

	Compounds referable to the type H^6O^3.	Compounds referable to the type H^8O^4.	Compounds referable to the type $H^{10}O^5$.	Compounds referable to the type $H^{12}O^6$.	Compounds referable to the type $H^{14}O^7$.	Compounds referable to the type $\left.\begin{matrix}H^8O^4\\HCl\end{matrix}\right\}$.	Compounds referable to the type $\left.\begin{matrix}H^4O^2\\H^3N\end{matrix}\right\}$	Compounds referable to the type $\left.\begin{matrix}H^6O^3\\H^3N\end{matrix}\right\}$.	Compounds referable to the type $\left.\begin{matrix}H^4O^2\\HCl\\H^3N\end{matrix}\right\}$.
Compounds containing the radicle *ethylene*, $(C^2H^4)''$.	$\left.\begin{matrix}(C^2H^4)^2\\H^2\end{matrix}\right\}O^3$ Lourenço.	$\left.\begin{matrix}(C^2H^4)^3\\H^2\end{matrix}\right\}O^4$ Wurtz, Lourenço.	$\left.\begin{matrix}(C^2H^4)^4\\H^2\end{matrix}\right\}O^5$ Wurtz Lourenço.	$\left.\begin{matrix}(C^2H^4)^5\\H^2\end{matrix}\right\}O^6$ Wurtz, Lourenço.	$\left.\begin{matrix}(C^2H^4)^6\\H^2\end{matrix}\right\}O^7$ Lourenço.		$\left.\begin{matrix}(C^2H^4)^2\\H^3\end{matrix}\right\}\begin{matrix}O^2\\N\end{matrix}$ Wurtz.	$\left.\begin{matrix}(C^2H^4)^3\\H^3\end{matrix}\right\}\begin{matrix}O^3\\N\end{matrix}$ Wurtz.	
Compounds containing the radicle *glycolyl*, $(C^2H^2O)''$.	$\left.\begin{matrix}(C^2H^2O)^2\\H^2\end{matrix}\right\}O^3$ Wurtz, Heintz	$\left.\begin{matrix}(C^2H^2O)^2\\(C^2H^4)H^2\end{matrix}\right\}O^4$ Wurtz.							
Compounds containing the radicle *lactyl*, $(C^3H^4O)''$.	$\left.\begin{matrix}(C^3H^4O)^2\\H^2\end{matrix}\right\}O^3$ Pelouze. $\left.\begin{matrix}(C^3H^4O)^2\\(C^2H^5)H\end{matrix}\right\}O^3$ Wurtz and Friedel.	$\left.\begin{matrix}(C^3H^4O)^3\\(C^2H^5)H\end{matrix}\right\}O^4$ Wurtz and Friedel. $\left.\begin{matrix}(C^3H^4O)^3\\(C^2H^5)^2\end{matrix}\right\}O^4$ Wurtz and Friedel. $\left.\begin{matrix}(C^3H^4O)^2\\(C^4H^4O^4)^2\\(C^2H^5)^2\end{matrix}\right\}O^4$ Wurtz & Friedel.							
Compounds containing the radicle *anisalyl*, $(C^8H^8)''$.							$\left.\begin{matrix}(C^8H^8)^2\\H^3\end{matrix}\right\}\begin{matrix}O^2\\N\end{matrix}$ Cannizzarro.		
Compounds containing the radicle *sulphuryl*, $(SO^2)''$.	$\left.\begin{matrix}(SO^2)^2\\H^2\end{matrix}\right\}O^3$ (Nordhausen sulphuric acid).						$\left.\begin{matrix}(SO^2)^2\\(C^6H^5)H^2\end{matrix}\right\}\begin{matrix}O^2\\N\end{matrix}$ Carius. $\left.\begin{matrix}(SO^2)^2\\(C^7H^7)H^2\end{matrix}\right\}\begin{matrix}O^2\\N\end{matrix}$ Carius. $\left.\begin{matrix}(SO^2)^2\\(C^9H^{11})H^2\end{matrix}\right\}\begin{matrix}O^2\\N\end{matrix}$ Carius.		
Compounds containing the radicle *glyceryl*, $(C^3H^5)'''$.		$\left.\begin{matrix}(C^3H^5)^2\\H^2\end{matrix}\right\}O^4$ Lourenço.	$\left.\begin{matrix}(C^3H^5)^2\\H^4\end{matrix}\right\}O^5$ Lourenço. $\left.\begin{matrix}(C^3H^5)^2\\(C^2H^5)^3H\end{matrix}\right\}O^5$ Reboul and Lourenço.	$\left.\begin{matrix}(C^4H^5)^3\\H^3\end{matrix}\right\}O^6$ Lourenço.	$\left.\begin{matrix}(C^3H^5)^3\\H^5\end{matrix}\right\}O^7$ Lourenço. $\left.\begin{matrix}(C^3H^5)^3\\(C^2H^5)^4H\end{matrix}\right\}O^7$ Reboul and Lourenço.	$\left.\begin{matrix}(C^3H^5)^2\\(C^2H^5)^2\\H\end{matrix}\right\}\begin{matrix}O^4\\Cl\end{matrix}$ Reboul and Lourenço.			$\left.\begin{matrix}(C^3H^5)^2\\H^2\end{matrix}\right\}\begin{matrix}O^2\\Br\\N\end{matrix}$ Berthelot and de Luca.
Compounds containing the radicle *phosphoryl*, $(PO)'''$.		$\left.\begin{matrix}(PO)^2\\Na^2\end{matrix}\right\}O^4$ Maddrell. (Insoluble metaphosphate.)	$\left.\begin{matrix}(PO)^2\\Na^4\end{matrix}\right\}O^5$ Clark. (Pyrophosphate.)	$\left.\begin{matrix}(PO)^3\\Na^3\end{matrix}\right\}O^6$ Fleitmann and Henneberg.					

Classification according to Types (continued).

	Compounds referable to the type H^9N^3.	Compounds referable to the type $H^{12}N^4$.
Compounds containing the radicle *ethylene*, $(C^2H^4)''$ (*continued*).	$\left.\begin{matrix}(C^2H^4)^2\\ H^5\end{matrix}\right\}N^3$	$\left.\begin{matrix}(C^2H^4)^3\\ H^6\end{matrix}\right\}N^4$
	$\left.\begin{matrix}(C^2H^4)^2\\ (C^2H^5)^2\\ H^3\end{matrix}\right\}N^3$	$\left.\begin{matrix}(C^2H^4)^3\\ (C^2H^5)^6\end{matrix}\right\}N^4$
	$\left.\begin{matrix}(C^2H^4)^2\\ (C^2H^5)^3\\ H^2\end{matrix}\right\}N^3$	$\left.\begin{matrix}(C^2H^4)^5\\ (C^2H^5)^2\end{matrix}\right\}N^4$
	$\left.\begin{matrix}(C^2H^4)^3\\ H^3\end{matrix}\right\}N^3$	$(C^2H^4)^6N^4$
	$\left.\begin{matrix}(C^2H^4)^3\\ (C^2H^5)^3\end{matrix}\right\}N^3$	
	Hofmann.	Hofmann.

A little reflection upon what has been said (p. 1017) on the nature of compound radicles, and on the sense in which they are employed, will make it clear that a classification of compounds by means of them, according to types, such as that illustrated in the two tables given, pp. 1018, 1019, 1021, 1022, expresses all we know of their general chemical properties. For the classification of a number of substances as containing the same radicle, expresses that they are mutually convertible by comparatively simple processes, that is, that they are *genetically* related,—while the classification of any set of bodies by reference to the same type, expresses that they are capable of undergoing similar transformations, and are therefore *functionally* related. All our strictly chemical knowledge, however, consists in a knowledge (1) of the nature and proportion of the elements of which substances are composed; (2) of their genetic relations, or of the bodies from which they can be formed, or to which they can give rise; and (3) of their chemical functions, or the transformations which they cause or undergo when they react with other bodies. In the foregoing pages, we have accordingly endeavoured to point out the leading principles which must be kept in view in classifying chemical substances with reference to considerations of each of these three kinds, considering however at the greatest length the classification of bodies according to their composition; partly because much less attention has been paid to this subject, in the existing literature of chemistry, than to their genetic and functional relations, but chiefly because composition is the most fundamental of all chemical properties, and the manner in which all other chemical properties depend upon it is the fundamental problem of chemistry. Throughout, we have endeavoured to distinguish between ideas and mere forms of expression, rendered convenient by the existing state of the science.

The order and system which has been followed in this article, has made it impossible to trace the historical development of the ideas therein set forth. The following list of Memoirs of theoretical importance will be of assistance to such readers as wish to trace that development from the birth of Organic Chemistry to the present time; many other memoirs of equal importance with some of those enumerated, might have been quoted; but in a large number of these, references are given which will serve as a guide to those who wish to pursue the subject further.

Lavoisier (*Compound radicles*), Traité élémentaire de Chimie (edit. 1789), i. 197, 209.

Dumas and Boullay (*Compound ethers*), Ann. Ch. Phys. xxxvii. 15 (1828).

Wöhler and Liebig (*Benzoyl compounds*), Ann. Ch. Pharm. iii. 249 (1832); Ann. Ch. Phys. li. 273.

Berzelius (*Radicle of the benzoic compounds*), Ann. Ch. Pharm. iii. 282; Ann. Ch. Phys. li. 308.

Berzelius (*Radicles of alcohol and its derivatives*), Jahresber. (1833), xiii. 189; Pogg. Ann. xxviii. 617; Ann. Ch. Phys. liv. 5; extract, Ann. Ch. Pharm. vi. 173.

Liebig (*Ethyl*), Handwörterb. d. Chemie (1ste Auflage), article *Æther;* Ann. Ch. Pharm. ix. 1; Pogg. Ann. xxxi. 321; Ann. Ch. Phys. lv. 113 (1834).

Liebig (*Acetyl, constitution of acetic acid*, &c.), Ann. Ch. Pharm. xiv. 133 (1835); Pogg. Ann. xxxvi. 275.

Dumas (*Substitution*), Ann. Ch. Phys. lvi. 143 (1835); Traité de Chimie appliquée aux Arts, v. 99; J. pr. Chem. vii. 293.

Laurent (*Nucleus theory*), Ann. Ch. Phys. lxi. 125 (1836).

Gerhardt (*Conjugated compounds*), *ibid.* lxxii. 184 (1838).

Dumas (*Substitution*), Compt. rend. x. 149; Ann. Ch. Pharm. xxxiii. 259 (1839).

Gerhardt (*Atomic weights of oxygen, carbon, &c.*), Ann. Ch. Phys. [3] vii. 129; viii. 238; Précis de Chimie organique (1844), i. 47.

Gerhardt (*Homology*), Précis, ii. 489.

Laurent (*Law of even numbers of atoms; nature of the elements in the free state; monads and dyads*), Ann. Ch. Phys. [3] xviii. 266 (1846); Chemical Method, 46—96, *et passim.*

Wurtz (*Compound ammonias*), Compt. rend. xxviii. 233, 323 (1849); xxix. 169; Ann. Ch. Phys. [3] xxx. 443; Chem. Soc. Qu. J. iii. 90.

Hofmann (*Compound ammonias*), Phil. Trans. 1850, i. 93; Chem. Soc. Qu. J. iii. 279.

Williamson (*Mixed ethers, etherification*), Chem. Soc. Qu. J. iv. 106, 229 (1851).

Williamson (*Constitution of salts*), Chem. Soc. Qu. J. ix. 350 (1851).

Gerhardt and Chancel (*Constitution of organic compounds*), Compt. chim. (1851), vii. 65.

Gerhardt (*Basicity of acids*), Compt. chim. (1851), vii. 129.

Gerhardt (*Anhydrous organic acids; classification by types*), Compt. rend. xxxiv. 755, 902 (1852); Chem. Soc. Qu. J. v. 127, 226; more fully Ann. Ch. Phys. [3] xxxvii. 285; Dumas's Report, Compt. rend. xxxvi. 505.

Berthelot (*Synthesis of fats; nature of glycerine*), Ann. Ch. Phys. xli. 216 (1853—54).

Odling (*Constitution of salts; polyatomic radicles*), Chem. Soc. Qu. J. vii. 1 (1854).

Wurtz (*Theory of glycerine-compounds; polyatomic radicles*), Ann. Ch. Phys. [3] xliii. 493 (1855).

Wurtz (*Mixed radicles*), *ibid.* xliv. 275.

Gerhardt and Chiozza (*Amides*), *ibid.* xlvi. 129 (1855—56).

H. L. Buff (*Polyatomic radicles*), Proc. Roy. Soc. viii. 188 (1856).

Wurtz (*Diatomic alcohols*), Compt. rend. xliii. 199; Ann. Ch. Pharm. c. 110; more fully, Ann. Ch. Phys. [3] lv. 400 (1856—59).

Kekulé (*Mixed types, radicles, &c.*), Ann. Ch. Pharm. civ. 129 (1857).

Kekulé (*Ditto; tetratomic character of carbon*), *ibid.* cvi. 129 (1858).

Couper (*Atomicity of carbon and oxygen*), Ann. Ch. Phys. [3] liii. 504 (1858); Ann. Ch. Pharm. cx. 46 (here followed by critique by Buttlerow, 1859).

Kolbe (*Constitution of lactic acid*), Ann. Ch. Pharm. cix. 257 (1859); same subject, *ibid.* cxiii. 223 (1860).

Foster (*Nature of radicles and types*), Brit. Assoc. Reports, 1859, 1.

Wurtz (*Basicity of acids*), Ann. Ch. Phys. [3] li. 342 (1859).

Cahours (*Combining capacity of the elements; limits of combination*), Ann. Ch. Phys. [3] lviii. 5 (1860).

Frankland (*Same subject*), Chem. Soc. Qu. J. xiii. 177 (1860).

Wurtz (*Constitution of lactic acid*), Ann. Ch. Phys. [3] lix. 161 (1860).

Cahours (*Same subject*), Ann. Ch. Phys. [3] lxii. 257 (1861).

Buttlerow (*Atomicity of the elements*), Zeitschr. Chem. Pharm. iv. 549 (1861).

Erlenmeyer (*Same subject*), *ibid.* v. 18 (1862).

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CLAUSTHALITE. Native selenide of lead. (See Lead.)

CLAY. This term is applied to hydrous silicates of aluminium, produced for the most part by the decomposition of felspar rocks, and generally mixed with small quantities of other substances, chiefly lime, magnesia, and oxide of iron. The clays exhibit the following general characters:—They are opaque, non-crystallised bodies, sufficiently soft to be scratched by iron; they have a dull or even earthy fracture; they exhale, when breathed on, a peculiar smell called argillaceous. The clays form with water a plastic paste, possessing considerable tenacity, which hardens with heat, so as to strike fire with steel. Marls and chalks also soften in water, but their paste is not tenacious, nor does it acquire a siliceous hardness in the fire. The affinity of the clays for moisture is manifested by their sticking to the tongue, and by the intense heat necessary to make them perfectly dry. Those which contain iron turn red when burnt. Clay is often mixed with quartz, and contains fine particles of felspar, mica, and beryl, showing that it has been produced by the decomposition of felspar or granite.

The principal varieties of clay are the following:

1. *Porcelain earth*, the kaolin of the Chinese.—This mineral is friable, meagre to the touch, and, when pure, forms with difficulty a paste with water. It is infusible in a porcelain furnace. It is of a pure white, verging sometimes upon the yellow or flesh-red. Some varieties exhibit particles of mica, which betray their origin to be from felspar or graphite granite. Porcelain clay scarcely adheres to the tongue. Specific gravity 2·2. The average composition of kaolin, when separated from free silica and undecomposed felspar, is 47 per cent. silica, 40 alumina, and 13 water, agreeing with the formula $Al^4O^3.2SiO^2 + 2$ aq. It may be supposed to be formed from orthoclase, $K^2O.Al^4O^3.6SiO^2$, by abstraction of the whole of the potash and $\frac{2}{3}$ of the silica, and addition of 2 at. water. Some varieties, however, exhibited a different composition; thus the kaolin of Passau contains, according to Fuchs, 43·65 per cent. SiO^2, 35·93 Al^4O^3, 1·00 Fe^4O^3, and 18·50 water, besides 0·88 carbonate of calcium, a composition which may be approximately represented by the formula $4Al^4O^3.9SiO^2 + 12$aq. Porcelain clay from Gutenberg, near Halle, contains, according to Bley, 39·02 SiO^2, 45·00 Al^4O^3, and 10·00 water, together with 0·07 carbonate of calcium, 3·32 carbonate of magnesium, and 0·19 sesquioxide of iron, agreeing approximately with $2Al^4O^3.3SiO^2 + 3$aq. (*Rammelsberg's Mineralchemie*, p. 574). In two specimens of Chinese kaolin, Ebelmen and Salvétat (Ann. Ch. Phys. xxxi. 257) found 73·4 and 80·7 SiO^2, 44·5 Al^4O^3, 14·4 and 12·0 water; in these the quantity of silica is twice as great, in proportion to the alumina, as in the ordinary formula of kaolin (Dana, ii. 250). Kaolin is found in primitive mountains, amid blocks of granite, forming interposed strata. Kaolins are sometimes preceded by beds of a micaceous rock of the texture of gneiss, but red and very friable. This remarkable disposition has been observed in the kaolin quarries of China, in those of Alençon,and of St. Yrieux, near Limoges. The Chinese and Japanese kaolins are whiter and more unctuous to the touch than those of Europe. The Saxon has a slight tint of yellow or carnation, which disappears in the fire, and therefore is not owing to metallic impregnation. At St. Yrieux, the kaolin is in a stratum, and also in a vein, amid blocks of granite, or rather the felspar rock which the Chinese call *petuntze*. The Cornish kaolin is very white and unctuous to the touch, and is obviously formed by the disintegration of the felspar of granite.

2. *Potters' clay*, or *plastic clay*.—The clays of this variety are compact, smooth, and almost unctuous to the touch, and may be polished by the finger when they are dry. They have a great affinity for water, form a tenacious paste, and adhere strongly to the tongue. The paste of some is even slightly transparent. They acquire great solidity, but are infusible in the porcelain furnace. This property distinguishes them from the common clays employed for coarse earthenware. Some of them remain white, or become so in a high heat; others turn red. Specific gravity about 2. The slaty potters' clay of Werner has a dark ash-grey colour; principal fracture imperfectly conchoïdal, cross fracture earthy; fragments tabular, rather light; it feels more greasy than common potters' clay. Vauquelin's analysis of the plastic clay of Forges-les-Eaux, employed for making glass-house pots, as well as pottery, gave 16 alumina, 63 silica, 1 lime, 8 iron, and 10 water. Another potters' clay gave 33·2 and 43·5, of alumina and silica, with 3·5 lime.

Fire-clay is a very refractory plastic clay, much used in the manufacture of fire-bricks, glass-house pots, &c. In this country it lies immediately beneath the coal, each bed of which rests upon a stratum of this clay, hence called in the mining districts *under-clay*. The Stourbridge clay is of this character. (See FIRE-CLAY.)

3. *Loam*.—This is an impure potters' clay mixed with mica and iron ochre. Colour yellowish-grey, often spotted yellow and brown. Massive, with a dull glimmering lustre from scales of mica. Adheres pretty strongly to the tongue, and feels slightly greasy. Its density is inferior to the preceding.

4. *Variegated clay* is striped or spotted with white, red, or yellow. Massive, with an earthy fracture, verging on slaty. Shining streak. Very soft, sometimes even friable. Feels slightly greasy, and adheres a little to the tongue. Sectile. It is found in Upper Lusatia.

5. *Slate clay*.—Colour grey, or greyish-yellow. Massive. Lustre dull or glimmering from interspersed mica. Fracture slaty, approaching sometimes to earthy. Fragments tabular. Opaque, soft, sectile, and easily broken. Specific gravity 2·6. Adheres to the tongue, and breaks down in water. It is found along with coal, and in the floetz trap formation.

6. *Claystone.*—Colour grey, of various shades, sometimes red, and spotted or striped. Massive. Lustre dull, with a fine earthy fracture, passing into fine-grained uneven, slaty, or splintery. Opaque, soft, and easily broken. Does not adhere to the tongue, and is meagre to the touch. It has been found on the top of the Pentland hills in Scotland, and in Germany.

7. *Adhesive slate.*—Colour light greenish-grey. Internal lustre dull; fracture in the large, slaty; in the small, fine earthy. Fragments slaty. Opaque. Streak shining. Sectile. Easily broken or exfoliated. Adheres strongly to the tongue, and absorbs water rapidly, with emission of air bubbles and a crackling sound. It is found at Montmartre, near Paris, between blocks of impure gypsum, in large straight plates like sheets of pasteboard; also at Menilmontant, enclosing menilite. Klaproth's analysis gives 62·5 silica, 8 magnesia, 0·5 alumina, 0·25 lime, 4 oxide of iron, 22 water, and 0·75 charcoal. Its specific gravity is 2·08.

8. *Polishing slate* of Werner.—Colour cream-yellow, in alternate stripes. Massive. Lustre dull. Slaty fracture. Fragments tabular. Very soft, and adheres to the tongue. Smooth, but meagre to the touch. Specific gravity in its dry state 0·6; when imbued with moisture 1·9. It has been found only in Bohemia. Its constituents are, 79 silica, 1 alumina, 1 lime, 4 oxide of iron, and 14 water.

9. *Common clay* may be considered to be the same as *loam.*—Besides the above, we have the analyses of some pure clays, the results of which show a very minute quantity of silica, and a large quantity of sulphuric acid. Thus, in one analysed by Bucholz, there was 1 silica, 31 alumina, 0·5 lime, 0·5 oxide of iron, 21·5 sulphuric acid, 45 water, and 1·5 loss. Simon found 19·35 sulphuric acid in 100 pts. These clays must be regarded as basic sulphates of aluminium. U.

For analysis of various clays, see *Ure's Dictionary of Arts, Manufactures and Mines,* i. 691.

CLAY-SLATE. *Argillaceous schist;* the *Argillite* of Kirwan.—Colour bluish-grey and greyish-black of various shades. Massive. Internal lustre shining or pearly. Fracture foliated. Fragments tabular. Streak greenish-white. Opaque. Soft. Sectile. Easily broken. Sonorous when struck with a hard body. Specific gravity 2·7. Its constituents are 48·6 silica, 23·5 alumina, 1·6 magnesia, 11·3 sesquioxide of iron, 0·5 oxide of manganese, 4·7 potash, 0·3 carbon, 0·1 sulphur, 7·6 water and volatile matter. Clay-slate melts easily before the blowpipe into a shining scoria. This mineral is extensively distributed, forming part of both primitive and transition mountains. The great beds of it are often cut across by thin seams of quartz or carbonate of lime, which divide them into rhomboïdal masses. Good slates should not imbibe water. If they do, they soon decompose by the weather. U.

CLAY IRON-STONE. See Iron.

CLAYITE. A mineral from Peru, occurring crystallised and as a crust $\frac{3}{8}$ of an inch thick on quartz. It appears to be composed of the sulpharsenites of copper and sulphantimonites of copper and lead. The crystals belong to the regular system, being combinations of the tetrahedron with the rhombic dodecahedron. Colour blackish-grey. Streak the same. Lustre metallic. Hardness = 2·5. Sectile. Melts easily before the blowpipe, and gives the reactions of lead, arsenic, and antimony. With soda it yields a metallic globule, which becomes dull on cooling. Possibly a pseudomorph of fahl-ore. (W. J. Taylor, Sill. Am. J. [2] xxix. 367.)

CLEAVAGE OF CRYSTALS. See Crystallography.

CLEAVLANDITE. Soda-felspar. (See Felspar.)

CLEOPHANE. Syn. with blende or native sulphide of zinc. (See Zinc).

CLEMATIS-CAMPHOR. The young branches of *Clematis flammula, Cl. vitalba, Cl. viticella, Cl. erecta,* &c., yield by distillation with water, a liquid which has a sharp taste, a pungent odour of radish, and reddens the skin; when exposed to the air, it loses its acidity, and if left to stand in closed vessels, deposits white scales and flocks of clematis-camphor. (Braconnot, Ann. Ch. Phys. vi. 734.)

CLEMATITIN. A bitter substance, perhaps $C^9H^{10}O^6$, obtained by Walz from the root of *Aristolochia clematitis* (i. 357).

CLINGMANNITE. Syn. with Margarite (*q. v.*)

CLINKSTONE or **PHONOLITE** is a compact felspathic rock, of greyish colour and smooth fracture, clinking when struck with a hammer, somewhat like a metal. Specific gravity = 2·2 – 2·4.

CLINOCHLORE. A mineral having the same composition as chlorite (i. 913), but differing from it in crystalline form, inasmuch as it belongs to the trimetric system, whereas chlorite is rhombohedral. The crystals of clinochlore are hemihedral, and have a micaceous structure, the crystallising planes often forming equilateral triangles. It is optically biaxial, the angle between the axes being 84° 30′ (or 80° to 86°); the plane of the axes is perpendicular to the cleavage-surface, but the two axes are unequally inclined to this surface, one at 54° the other at 30°. It occurs in large crystals, usually having a rhombohedral aspect, and in plates; often compounded, the crystals giving a second pair of optical axes, making an angle of 60° with the other. Specific gravity about 2·714. Hardness 2—2·5. Lustre somewhat pearly. Colour olive-green. Transparent, unless in thick plates. Somewhat elastic.

Analyses.—*a*, *b*, from Chester county, Pennsylvania, by W. J. Craw (Sill. Am. J. [2] xiii. 222); *c*, from Lisgau, Bavaria, Kobell (Gel. Anzeige, 1854, No. 43):

	SiO^2	Al^4O^3	Fe^4O^3	Cr^4O^3	Mg^2O	H^2O		
a.	31·34	17·47	3·85	1·69	33·44	12·60		= 100·39
b.	31·78		22·71		33·64	12·60		= 100·72
c.	33·49	15·87	2·30	0·55	32·94	11·50	Fe^2O 4·25	= 100·40

Before the blowpipe it behaves like chlorite, showing traces of fusion on the edges. (Dana, ii. 294.)

CLINOCLASE. Syn. with ABICHITE (i. 1).

CLINTONITE. *Seybertite, Holmesite, Chrysophane.*—A silicate found at Amity, New York, in limestone connected with serpentine, together with augite, hornblende, spinel, and graphite. It forms small tabular crystals or foliated masses, sometimes lamellar, radiate. Structure thin, foliated, or micaceous, parallel to the base. According to Breithaupt, the crystals are monoclinic, with the angles between the lateral planes = 94°. Specific gravity = 3—3·1. Hardness = 4—5. Lustre pearly, submetallic. Colour reddish-brown, yellowish or copper-red. Streak uncoloured, or slightly yellowish or greyish. Folia brittle.

Closely allied to clintonite are *Xanthophyllite*, from Slatoust in the Ural, where it occurs in implanted globules, and in columnar or lamellar individuals, sometimes enclosing small hexagonal crystals secondary to a rhombic prism, and *Disterrite* or *Brandisite*, occurring in the Fassa valley, Tyrol, in hexagonal prisms of specific gravity 3·042—5·051, and hardness = 5 on the base, 6—6·5 on the sides.

Analyses.—*a*, *Seybertite*, by Clemson (Sill. Am. J. xxiv. 171).—*b*, *Holmesite*, by Richardson (Rec. Gen. Sci. May, 1836).—*c*, Clintonite, by Brush (Sill. Am. J. [2] xviii. 407).—*d*, *Xanthophyllite*, by G. Rose (Pogg. Ann. i. 654).—*d*, *Disterrite* or *Brandisite*, by Kobell (J. pr. Chem. xli. 154):

	SiO^2	ZrO^2	Al^4O^3	Fe^4O^3	Mn^2O	Mg^2O	Ca^2O	K^2O	Na^2O	H^2O	F	
a.	17·0	—	37·6	5·5	—	24·3	10·7	—	—	3·6	—	= 99·7
b.	19·35	2·05	44·75	4·80	1·35	9·05	11·45	—	—	4·55	0·90	= 98·25
c.	20·18	0·19	38·90	3·87	—	21·25	13·52	0·29	1·14	1·04	—	= 100·41
d.	16·30	—	43·95	2·91	—	19·31	13·26	—	0·61	4·33	—	= 100·57
e.	20·00	—	43·22	3·60	—	25·01	4·00	0·57	—	3·60	—	= 100

These results may be approximately represented by the following formulæ, in which M denotes a uni-equivalent and R a sesquiequivalent metal:—

Clintonite (Seybertite, Holmesite) . $2M^2O.3SiO^2 + 2(3M^2O.2R^4O^3)$
Xanthophyllite . . . . . . $2M^2O.3SiO^2 + 3(3M^2O.2R^4O^3) + 3aq.$
Disterrite . . . . $2M^2O.3SiO^2 + 4(M^2O.R^4O^3) + 2aq.$

It is doubtful whether either of these minerals has been found in an unaltered state.

Clintonite is infusible before the blowpipe, but loses its brown colour and becomes opaque; heated in a flask it gives off neutral water. It is completely decomposed by hydrochloric acid.

Xanthophyllite yields green glasses with fluxes: it is decomposed by acids, like clintonite, but much less easily.

Disterrite when heated gives off water, which is neutral or alkaline, according as the specimen is fresh or has turned red-brown by weathering. Before the blowpipe it becomes turbid and greyish-white, but does not fuse; with fluxes it gives the reactions of iron and silica. It is not sensibly attacked by hydrochloric acid; but sulphuric acid decomposes it when heated with it for some time. (*Rammelberg's Mineralchemie*, p. 848.—Dana, ii. 297.)

CLOUDS are masses of air which contain innumerable minute particles of suspended water condensed from a state of vapour, and thus assume the appearance of white or misty bodies. The forms of clouds, which of course depend on the form and motions of the mass of air, were first properly classified by Howard, (*Rees' Cyclopædia*, art. CLOUD; *Nicholson's Journal*, 1811, xxx. 35—62; or *Howard's Climate of London*, 2nd ed. vol. i.), whose arrangement we may thus shortly describe.

Cirrus.—Parallel, flexuous, or diverging fibres, commonly called *mare-tails*, occurring most distinctly in the higher regions of the atmosphere, but sometimes originating from large masses of other cloud at lower elevations. The adjective *cirrose* may be applied to any streaked appearance in clouds.

Cumulus.—Convex or conical heaps, increasing upward from a horizontal base. This is the most abundant form of cloud, generally appearing during the day at a moderate elevation, and moving along with the current next the earth.

Stratus.—A widely extended continuous horizontal sheet, either lying upon the surface of the earth as a mist, or elevated at any height in the atmosphere.

Cirrostratus.—Stratus streaked with the fibres of the cirrus. This form of cloud, generally occurring at a great elevation, and consisting, therefore, of particles of ice, is the cause of solar and lunar halos, and also of the parhelion and paraselene.

Cumulostratus.—A cumulus the summit of which spreads laterally, producing an anvil-shaped cloud. This kind of cloud is very likely to turn to the following:

Nimbus, Cumulo-cirro-stratus, Rain, or *Thundercloud* is a cloud or system of clouds forming a great sheet or mass, mostly cumulose, but with lateral stratose extensions, and with tufts of cirrus spreading from the summit. It indicates a great disturbance of the atmosphere, caused by a violent upward current in the centre of the cloud, and is generally accompanied by wind or squalls.

The following further statements are on the authority of Howard.

The *cumulus* has the densest structure, and is formed in the lower atmosphere. A small irregular spot first appears, and is, as it were, the nucleus on which the mass increases. The lower surface continues irregularly plane, while the upper rises into conical or hemispherical heaps, which may afterwards long continue nearly of the same bulk, or rapidly rise into mountains. They will begin, in fair weather, to form some hours after sunrise, arrive at their maximum in the hottest part of the afternoon, then go on diminishing, and totally disperse about sunset. Previous to rain, the cumulus increases rapidly, appears lower in the atmosphere, and with its surface full of loose fleeces or protuberances. The formation of large cumuli to leeward in a strong wind indicates the approach of a calm with rain. When they do not disappear or subside about sunset, but continue to rise, thunder is to be expected in the night.

The *stratus* has a mean degree of density, and is the lowest of clouds, its inferior surface commonly resting on the earth or water. This is properly the cloud of night, appearing about sunset. It comprehends all those creeping mists, which in calm weather ascend in spreading sheets (like an inundation of water), from the bottom of valleys and the surfaces of lakes and rivers. On the return of the sun, the level surface of this cloud begins to put on the appearance of cumulus, the whole at the same time separating from the ground. The continuity is next destroyed, and the cloud ascends and evaporates, or passes off with the appearance of the nascent cumulus. This has long been regarded as a prognostic of fair weather.

The *cirrus* having continued for some time increasing or stationary, usually passes either to the cirro-cumulus or the cirro-stratus, at the same time descending to a lower station in the atmosphere. This modification forms a very beautiful sky, is frequent in summer, and attendant on warm and dry weather. The *cirro-stratus*, when seen in the distance, frequently gives the idea of shoals of fish. It precedes wind and rain, is seen in the intervals of storms, and sometimes alternates with the cirro-cumulus in the same cloud, when the different evolutions form a curious spectacle. A judgment may be formed of the weather likely to ensue, by observing which modification prevails at last.

Howard did not explain the special causes of forms of clouds above described, nor can we point to more than one or two attempts at all sound and scientific to accomplish this. In two papers, however, in the *Philosophical Magazine* (4th ser. xiv. 22; xv. 241), it is shown, by analogical experiments with liquids, that the cirrus arises from the *interfiltration* of masses of air saturated with moisture, and not in equilibrium; the stratus, from mixture or contact of layers of air tranquilly moving on or lying over each other, while the cumulus arises from the violent ascent of columns of air in the atmosphere. The nimbus, rain, or thundercloud appears to be formed in like manner.

Very little is known of the nature of clouds from which slow long-continued rain falls, as it so commonly does in London, but the cloud is probably for the most part stratose.

More particular accounts of the phenomena of the clouds and weather must be sought in works on meteorology, among which by far the most philosophical and reliable, is Sir J. Herschel's Essay on Meteorology (Encyc. Brit. 8th ed.). To this Essay we are indebted for some of the following remarks.

It is more within the province of the chemist to consider the nature of the *matter* of clouds. Meteorologists have generally assumed, as an unsupported dogma, that cloud particles are small vesicles or watery bubbles. Saussure, indeed, is said to have examined these vesicles in the mists of high mountains, and to have found them vary in size from $\frac{1}{4500}$ inch to the $\frac{1}{2780}$ inch, occasionally however attaining the size of a pea. Now although no observer is in general more deservedly trusted than Saussure, his unsupported announcements must not always be adopted as conclusive, and we are quite unaware of any one else having witnessed vesicles of appreciable size floating in the air and forming clouds or mists. It is also stated (*Graham's Elements*, 2nd ed. i. 314), that the vesicles may be observed by a lens of an inch focal length, over the dark surface of hot tea or coffee, mixed with an occasional solid drop, which contrasts with them. Having tried this, we witnessed a white dust of watery particles of uniform size, blowing about over the surface of the coffee, or rising in little wreaths and whirlwinds like dust on a windy day, but we saw no drops appearing solid as contrasted with the rest, and were inclined to consider them all solid particles of about the diameter of $\frac{1}{5000}$ inch. No one has ever suggested how the vesicles are formed, nor is it easy to conceive any possible mode of their formation.

In favour of the vesicular theory, it may be urged that rainbows are at least very seldom produced when the sun shines on cloud or on steam, although a rainbow is exhibited under such circumstances by the minutest rain and by spray from a fountain or waterfall. Sir J. Herschel suggests that the particles may be of an *order of smallness* comparable to the lengths of the light-undulations, which are on an average about $\frac{1}{50000}$ inch long. Hence, he infers, the refractions and reflections of light which cause the rainbow would not take place. (See also Raillard, *Comptes Rendus*, xliii. 906.)

The existence of vesicular vapour of water seems, however, to have been disproved by the microscopic observations of Dr. A. Waller (Phil. Trans. cxxxvii. [1847] p. 23), which later writers have overlooked. Steam being thrown upon a surface of Canada balsam, the particles of water became fixed and were easily examined in the microscope. It was concluded that whenever we are enabled to inspect the minutest particles of water arising from condensed steam or vapours, they consist of minute liquid globules without any appearance of internal cavity.

The suspension of the clouds is in no way mysterious, and arises only from the enormous comparative resistance which the air offers to the motion of a very minute body, as Prof. Stokes has lately shown (Cambridge Phil. Trans. vol. viii. ix.) A globule of water of the diameter of $\frac{1}{1000}$ inch, in falling through the air, would have the maximum velocity of about ·067 inch per second, which is quite inappreciable compared with the ascensional movement of the air, which is generally taking place in all large masses of cloud. The watery particles, or the air, generally both, must then be in motion in every cloud. (See also Phil. Trans. vol. lv. [1765] p. 162.)

No satisfactory reason has ever been given why the clouds only sometimes discharge rain, but it is not difficult to see that if all the particles were of equal size, they would all subside at exactly the same rate, and no collisions could take place. But if a further set of particles were precipitated of a different size they would move at a different rate, and encounter the other particles; many particles would thus coalesce into drops of sufficient size to fall rapidly, and receiving accretions in their passage through the air, reach the surface of the earth as rain. The coalescence of minute globules vastly diminishes their surface as compared with their bulk; it is easy then to understand how electric tension existing on the surface of cloud particles is so intensified when rain falls as to occasion lightning. This theory of the thundercloud was suggested as early as 1752 by Eeles (Phil. Trans. p. 527), and it is repeated in the papers in the *Philosophical Magazine* before referred to.

There are two principal ways in which cloud particles are produced:

1. A gas in changing its volume also changes its temperature, and may thus be unable to sustain in the gaseous state all the aqueous vapour which is diffused through it. Thus, if the air within the receiver of an air-pump be moist, a few strokes of the pump will produce a visible mist. In the atmosphere, by far the largest masses of clouds are thus produced by columns of air rising, and consequently expanding and growing cold as they rise. Fogs, it is also said, may be produced at the surface by sudden changes of barometric pressure.

2. Two masses of moist air of different temperatures will not, when mixed, sustain the whole of the contained vapour in the gaseous state: for the maximum tension of aqueous vapour varies in a higher ratio than the temperature. Hence the mean tension of vapour on mixing, will always be higher than the tension possible at the mean temperature, and vapour will be condensed until the two are equalised. Thus arise the cirrose and stratose forms of cloud, from the mixing of bodies of air under various circumstances.

Gases have but an inappreciable power of conducting heat. A cold surface may indeed condense vapour from the air, as in the formation of dew, but the water condensed will all attach itself to the cold surface, and no cloud-particles will be produced.

Dr. Tyndall having lately proved that gases may radiate heat, it is possible that clouds may be produced in the higher parts of the atmosphere by slow radiation. W. S. J.

CLOVES, OIL OF. *Gewürznelkenöl.*—This oil, obtained by distilling with water the buds and flower-stalks of the clove-tree, *Eugenia caryophyllata*, or *Caryophyllus aromaticus*, L., is a mixture of eugenic acid (*q. v.*) and a hydrocarbon, $C^{10}H^{16}$, isomeric with oil of turpentine. This hydrocarbon passes over with vapour of water, when the crude oil of cloves is distilled with potash-ley. It is highly refractive, has a density of 0·918 at 18° C., and boils at 142°—143°. It is not attacked by alkalis; it absorbs a large quantity of hydrochloric acid, and without forming a crystalline compound (Ettling, Ann. Ch. Pharm. lx. 68). Water distilled from cloves sometimes deposits nacreous scales of eugenin, a substance probably isomeric with eugenic acid.

According to Stenhouse (Ann. Ch. Pharm. xcv. 103), the so-called oil of cinnamon-leaf is likewise a mixture of eugenic acid and a hydrocarbon, $C^{10}H^{16}$. It has a density of 0·862, and boils at 160°—165° C.; it contains also a small quantity of benzoic acid.

CLOVORUBRIN. A resinous body produced by the action of sulphuric acid on oil of cloves.

CLUB MOSS. See Lycopodium.

CLUTHALITE. A mineral related to analcime (p. 210), occurring in flesh-red vitreous crystals in the amygdaloïd of the Kilpatrick Hills. Specific gravity = 2·166. Hardness = 3·5. Opaque or subtranslucent. Fragile. Contains 51·27 SiO^2, 23·56 Al^4O^3, 7·31 Fe^4O^3, 5·13 Na^2O, 1·23 Mg^2O, and 10·55 water = 99·05. (Thomson, *System of Mineralogy*, i. 339.)

CNICIN. *Centaurin.* (Morin, J. Chim. méd. iii. 105; Scribe, Compt. rend. xv. 803).—A bitter substance contained in *Centaurea benedictus* or *Cnicus benedictus* (Morin); also in the leaves of *Centaurea calcitrapa*, and in all bitter plants of the order *Compositæ*, sub-order *Cynarocephalæ* (Scribe). Morin first obtained it in an impure state by treating the alcoholic extract of *Centaurea benedictus* with ether, evaporating, precipitating with sub-acetate of lead, evaporating the filtered liquid after freeing it from lead, and treating the residue with ether and alcohol. It was afterwards obtained by Nativelle and further examined by Scribe.

Cnicin forms white transparent silky needles, inodorous, having a pure bitter taste, and neutral reaction, easily soluble in alcohol and wood-spirit, very little soluble in ether. The alcoholic solution deflects the plane of a polarised ray to the right; $[\alpha] = +130{\cdot}68°$ (Bouchardat). It is nearly insoluble in cold water, dissolves somewhat more easily in warm water. The solution is decomposed by continued boiling, becoming turbid and afterwards depositing a viscid body like turpentine.

Cnicin gives by analysis 62·9 per cent. carbon, 7·0 hydrogen, and 30·1 oxygen, whence have been deduced the three formulæ $C^{14}H^{18}O^5$, $C^{20}H^{26}O^7$, and $C^{28}H^{34}O^9$. They all agree pretty nearly with the analysis, but as there is no means of determining the atomic weight of cnicin, it is impossible at present to decide between them.

Cnicin submitted to dry distillation gives off vapours and becomes carbonised. Strong sulphuric acid dissolves cnicin with deep blood-red colour, the liquid becoming black when heated. Strong hydrochloric acid is coloured green by it; if heat be applied, the liquid turns brown, and oily drops collect on its surface, solidifying in a resinous mass on cooling.

COAGULUM is a term applied to any viscid or curdy mass separated from a liquid, as cheese from milk, the clot from blood, &c.

COAL. *Houille. Steinkohle.*—The vast masses of fossil fuel which are stored up within the bowels of the earth, and in particular constitute so essential an element of our national prosperity, are undoubtedly the result of complex chemical changes, acting under varying circumstances of temperature, pressure, moisture, &c., either upon vegetable matter growing on the spot, or upon the remains of plants collected by the drift of rivers, &c., into particular localities.

The vegetable origin of coal is beyond doubt, nor can there be any question as to the character of the flora of the carboniferous era, about 500 distinct species, including 250 ferns, having been recognised as belonging to that period.

The discovery of distinct ligneous structure in most kinds of coal appears, however, to be somewhat questionable; and although Bischof and others have entered into interesting and highly valuable speculations as to the precise changes, by virtue of which woody matter may be converted into coal, the microscopic and chemical examination of the substances themselves, do not afford direct *proof* of the accuracy of these conceptions.

The conversion of wood into coal, according to Bischof, may take place in four different ways, viz.:

1. By separation of carbonic acid and carburetted hydrogen.
2. " " " water.
3. " carburetted hydrogen and water.
4. " " " carbonic acid.

(For the formulæ representing these changes we refer the reader to *Bischof's Chemical and Physical Geology*, vol. i. p. 274, *et. seq.*)

"When wood or vegetable matter, then, is buried under circumstances which allow of the extrication of these substances from it, in the course of its decomposition, it *must* become converted into coal; the extreme result of the process being to give us, first anthracite, containing perhaps 94 per cent. of carbon, and finally graphite, which is either pure carbon itself, or that substance mingled with others which are here excluded from consideration, as not being among the elements of wood, and which it may have acquired from external sources during the process of conversion.

"The great quantities of carbonic acid gas (choke-damp), and carburetted hydrogen (fire damp) met with in coal mines, show the fact of the large extrication of these substances, and corroborates, if need were, this explanation. Reservoirs of these gases in a highly compressed state are often found to be pent up in the crevices and cavities of coal beds. Some beds of coal are so saturated with gas, that when they are cut into, it may be heard oozing from every pore of the rock, and the coal is called by the colliers 'singing coal.'" (Beete Jukes, *Manual of Geology.*)

The natural escape of light carburetted hydrogen, marsh-gas or fire-damp (CH^4), which frequently bursts forth in large quantities from the seams of coal or strata of fire-clay which divide them, is the frequent cause of those terrible accidents, of which the Lund Hill Colliery explosion in 1857, and the still more recent one at Burradon, have been the most calamitous upon record.

The sudden issue of gas from a *blower* in the colliery adjacent to that of Lund Hill is thus described. "The fire-clay of the floor of the seam was seen to heave at different points along the face, and presently large fractures were made in it, through which gas was ejected with great violence and with a sound very similar to the issue of steam at a high pressure from a boiler." Subsequent to the explosion at Lund Hill, the pent up gas still issuing within the mine in the higher parts of the workings supported two columns of water 30 feet high, one 10 feet and the other 11½ feet diameter, corresponding to a pressure of about 11 lbs. on the square inch. This gas in exploding renders unfit for respiration 10 times its own bulk of air: hence the "after damp" of the miner, the vitiated atmosphere produced by the explosion, often fatal to those working in other parts of the mine, or to those who descend into the pits without proper precautions, or until ventilation has been sufficiently re-established.

"The subjoined tables, given by Miller, give an idea of the composition of wood and will illustrate the progress of its decay. They also furnish a synoptic view of the composition of some of the principal varieties of coal, in the order of their occurrence in successive geological stages. The proportion of oxygen diminishes rapidly and that of hydrogen more slowly, as the coal passes from lignite towards anthracite, in which form it consists of nearly pure carbon."

Composition of Wood and Coal.

	Oak-wood. Miller.	*Decayed Oak.* Liebig.	*Dartmoor Peat.* Vaux.	*Mexican Asphalt.* Regnault.	*Lignite from Bovey.* Vaux.	*Boghead Coal.* Miller.
Specific gravity	·81		·849	1·063	1·129	1·196
Coke per cent.	21·3		29·30	9·0	30·8	30·23
Carbon	50·10	53·47	54·02	78·10	66·31	63·10
Hydrogen	6·07	5·19	5·21	9·30	5·62	8·91
Nitrogen	43·68	41·37	2·30	9·80	0·56	7·25
Oxygen			28·17		22·86	
Sulphur			·56		2·36	·96
Ash	·15		9·73	2·80	2·27	19·78

Composition of Coal.

	Lesmahagow Parrot Coal. Miller.	*Wigan Cannel.* Vaux.	*Caking Coal Newcastle.* Richardson.	*10 yard Wolverhampton.* Vaux.	*Newport Steam.* Miller.	*S. Wales Anthracite.* Vaux.
Specific gravity .	1·251	1·276	1·280	1·278	1·309	1·392
Coke per cent. .	43·3	60·36		59·21	75·10	92·10
Carbon . . .	73·44	80·07	86·75	78·57	81·47	90·39
Hydrogen . .	7·62	5·52	5·24	5·29	4·97	3·28
Nitrogen . .	11·761	2·12	6·61	1·84	1·63	0·83
Oxygen . . .		8·08		12·88	5·23	2·98
Sulphur . . .	1·145	1·50		·39	1·10	0·91
Ash . . .	6·034	2·70	1·40	1·03	5·51	1·61

The composition of coals varies largely, not only in respect of the relative proportions of carbon, hydrogen, oxygen and nitrogen which they contain, but also of the amount of extraneous matters which constitute the impurities of fuel. These consist of a variable amount of mineral matters which remain after combustion of the coal, as ash or "clinker."

The percentage of ash ranges from about 1 to 30 or 35, and in some coals, which are considered too poor to be brought to market, to even more than this quantity.

It consists chiefly of silicate of alumina, with variable amounts of oxide of iron. Vaux found also in many coals traces of lead and copper.

"We have in nature every gradation, from pure coal into a mere carbonaceous (commonly called bituminous) shale or 'batt' which often contains enough imflammable matter to give out flame and support combustion for a time when burnt with better coals, but soon passes into a lump of ash, unaltered in form and not retaining heat longer than a brickbat would under similar circumstances." Accordingly, the composition of the ash of coals closely resembles that of the batts, shales, or fire-clays which usually occur, either as strata above or below the coal, or in their "partings" between the several layers of the coal itself.

The following table exhibits the amount and composition of the ashes of several coals, as compared with that of fire-clays and "batts":

Composition of Coal-ash.

	Newcastle coal after deducting Suphuric acid. Taylor.	Porous Coal from Zwickau. Kremers.	Compact Coal from Zwickau. Kremers.	Average of five samples. Welsh. Phillips.	Average of five samples. Scotch. Phillips.	Blue Shale clay. Taylor.	Newcastle Fireclay. Richardson.	American Anthracite Fawn.	Ash of Bituminous Shale, Bilston, Staffordshire. Wills.
Silica . .	62·44	60·23	45·13	42·67	49 63	58·99	57·08	54·50	60·31
Alumina .	31·22	31·63	22·47	43·56	38·21	26·19	35·02	34·45	29·85
Sesquioxide iron . .	2·26	6·36	25·83		. .	. .	5·17	7·50	3·14
Lime .	·75	1·08	2·80	6·65	3·18	Fe^2O.10·25	1·63	2·25	2·19
Magnesia .	·85	·35	·52	1 08	1·41	·67	1·73	1·30	1·83
Potash .	2·48	. .	. .	. .	. .	1·54	. .	. .	2·12
Soda . .	. .	. .	·24	. .	. .	2·34	. .	. .	
Sulphuric acid (anhydrous) .	. .	. .	. .	4·46	6·26	. .	. .	. .	0·69
Sulphate of Calcium .	. .	·24	2·27						
Phosphoric acid (anhydrous) .	. .	. .	. .	·66	1·03	. .	. .	. .	traces.
Percentage of Ash .	1·36	1·74	1·89	8·15	. .	. .	. .	. .	Chlorine 0·06

Muspratt states that the ash of lignite varies from 1 to 60 per cent., averaging about 5, and that of bituminous coal 1 to 2 per cent. In addition to these substances, the mineral matter of coal contains a small but variable quantity of sulphur, not accounted for in the above analyses, but constituting a most important element as regards the value of fuel for domestic and technical uses. This remark applies more especially to the value of coals for metallurgical purposes, particularly for employment in the blast-furnace; the ironmaster, has learned to eschew such samples of ironstone as contain any considerable percentage of sulphur and phosphoric acid; but this precaution is wholly ineffectual, unless a like care be exercised in the selection of the fuel and fluxes which are to be introduced into the blast-furnace with the ore.

The presence of sulphur is equally detrimental in the manufacture of gas, some portion of it being always eliminated as sulphuretted hydrogen and bisulphide of carbon, the complete removal of which is a matter at once of great difficulty and of the highest necessity, while the frequent cases of spontaneous combustion of coals in the hold of vessels is probably due, in some measure, to the oxidation of the pyrites which they contain under the influence of a moist atmosphere.

A minor evil is the evolution, during combustion, of sulphurous acid, a gas which is not only noxious and hurtful to human life, but destructive to boilers, locomotive tubes, and so forth.

Some of the lower seams of the South Staffordshire coal beds, otherwise available as good fuel, are unused, because they contain an amount of sulphur which renders it impossible to bear the smell which they exhale during combustion; whence their local name of *stinking coal*.

The mean percentage of sulphur found in the government investigation, under Playfair and De la Beche, was as below:

Samples.	Coals.	Mean.
37	Welsh	1·42
8	Derbyshire	1·01
28	Lancashire	1·42
17	Newcastle	0·94
8	Scotland	1·45

The following are other determinations of sulphur in coals:—

	Mean.
4 samples from North Wales, Ruabon	·79
Lignite from Bovey (Vaux)	2·36
Boghead (Miller)	0·96
Wigan cannel (Vaux)	1·50
10 yard Wolverhampton	0·39
„ bottom	2·57
Newport steam coal (Miller)	1·10
Anthracite, South Wales (Vaux)	·91

"The frequent occurrence of iron pyrites in coal shows that its formation at the cost of organic remains is a very frequent phenomenon. This formation of iron pyrites can only be explained by the presence of sulphates; and so far as it goes on in the sea, only by the decomposition of sulphate of calcium.

The minor varieties of coal are almost infinite in number, and it is said that full a hundred different kinds are sent into the London market. The following appears to be as satisfactory a classification of the more important kinds as is possible, together with an indication of their characteristic differences, and of the localities whence they are obtained:—

1. LIGNITE or BROWN COAL generally retains in some degree its lamellar and woody structure. Yields a powdery coke in the form of the original lumps. Brittle, burns readily, but often contains from 30 to 40 per cent. water.

Occurs in England chiefly at Bovey Heathfield, in Devonshire, where it has long been used as fuel in the local potteries; the supply is now, however, falling off. Its other chief localities are Westphalia, the Hessian States, Lower Austria, Russia, Spain, Portugal, Italy, the Upper Missouri Valley, New Brunswick (impregnated with copper), Greenland, China, and the Burmese Empire, and in Central America in the province of Panama.

2. BITUMINOUS or CAKING COALS.—The most extensively diffused and valuable of English coals. These are of various shades of brown and black, emit much gas on heating, and hence are prized as "gas-coals;" they leave a coke more or less lustrous and fused, or *caked* together. Their fracture is generally uneven and their lustre resinous. The coals of this class are subdivided into:

Caking Coal, which splinters on heating, but the fragments then fuse together into a semi-pasty mass. Its chief sources are the Newcastle and Wigan districts, along the banks of the Tyne and Wear, and the north of the Tees.

Cherry Coal or *Soft Coal*.—Lustre very bright. Does not fuse. Ignites well and burns rapidly. Occurs in Glasgow, Staffordshire, Derbyshire, Nottingham, Lancashire, &c.

Splint, Rough or *Hard Coal.*—Black, and of glistening fracture. Does not ignite readily, but burns up to a clear hot fire, constituting a good house coal. Occurs in the Glasgow field, in Shropshire, Leicestershire, Warwickshire, Derbyshire, and at Nottingham, and constitutes in particular the bulk of the great coalfields of North and South Staffordshire.

Cannel Coal; Parrot coal of Scotland.—Of dense, compact, and even fracture, conchoïdal in every direction. Takes a polish like jet. Splinters in the fire and burns clearly and brightly. The chief localities in Great Britain are Wigan, and other parts of Lancashire, West Glasgow, and in smaller quantities at Coventry. It is found also in Kentucky.

The various kinds of bituminous coal constitute also the bulk of the immense coalfields of North America, compared with which the most extensive fields of the Old World are insignificant. These are the Alleghany or Appalachian field, and those of Pennsylvania, Illinois, New Brunswick, and Nova Scotia. In South America they occur in the province of Chili. They compose also the south side of the South Wales basin; are found in Connaught and Ulster, and on the European continent in Belgium, France, Prussia, Sweden, Russia, and Spain. Finally, the great coal range of New South Wales is supposed to belong to this class.

4. ANTHRACITE. STONE-COAL or CULM.—The densest, hardest, and most lustrous of all varieties. Burns with very little flame or smoke, but gives great heat. Contains very little volatile matter. Splinters when heated, and ignites with difficulty. Colour deep black, fracture lamellar, parallel to the bed of the deposit, conchoïdal in the cross fracture. Applied successfully to smelting, and much valued as a steam coal in the navy. Its most extensive deposit occurs over vast tracts of North America, chiefly in Pennsylvania. It constitutes also a large portion of the yield of the northwest portion of the South Wales coalfield. A further deposit occurs over a tract of about 12½ miles in Devonshire, in the neighbourhood of Barnstaple Bay and Bideford. Its other situations are Leinster and Munster in Ireland, and some districts of France, Sweden, and Portugal.

5. STEAM COAL approaches nearly to anthracite. It does not crumble into small pieces under friction, and is hence well adapted for stowage. It also emits little smoke, a point of great importance in naval warfare, where the smoke of ordinary coals would reveal the position of vessels to a distant enemy. Its chief locality is the north-west of the South Wales basin and the north of the Tyne and Blyth district.

In addition to the above-named varieties, we must mention the remarkable deposit of Bathgate, near Edinburgh, commonly known as the "Torbane hill mineral or Boghead cannel coal," respecting which a curious lawsuit arose upon the question whether or not the substance was to be considered as "coal." It is of a dull brown colour in the upper part, and black in the lower part of the seam, and of low specific gravity. It contains about 20 per cent. of aluminous ash, which remains after ignition in the form of the original lump, retaining 6 to 10 per cent of carbon. About 70 per cent., therefore, consists of volatile matter, whence the great value of the mineral for two purposes; 1st for gas making; 2nd for distillation, by Young's process, in close vessels at a low temperature, whereby a large number of liquid hydrocarbons of various densities and boiling points are obtained, fit respectively for illuminating and lubricating purposes, together with paraffin and other solid products.

The analyses already given fairly represent the ordinary composition of the several classes of coals.

Valuation of Coal.—A ready method of accurately estimating the general value of coal as fuel is yet a desideratum. Its elementary analysis affords the means of calculating its theoretical heating power; but it is found in practice that the amount of work indicated by this result can never be obtained, and further that the condition of mechanical division, draught of furnaces, and many other extraneous circumstances affect the result so largely, that the actual work obtained seldom bears any palpable relation to the theoretical indication.

The weight of water in pounds raised *one degree* in temperature by the combustion of 1 cubic inch of each of a large number of combustible substances, and also by such a weight of each as combines with 1 cubic inch of oxygen, has been determined by the direct experiments of Lavoisier, Laplace, Despretz, Dulong, Rumford, Regnault, Andrews, and others, the general principle of their methods consisting in the use of an apparatus wherein the entire heat of combustion was absorbed by a known weight of water, the whole arrangement being protected from the influence of external changes of temperature, and the increase of temperature of the water being known by the simultaneous indication of several delicate thermometers suspended in it. (See HEAT.)

The method of Berthier, though only approximative, affords useful indications when applied, with certain precautions, to various samples of the same class of coal or from the same mine.

It is based upon the reduction of oxide of lead by the carbon and hydrogen of the fuel, in fact the combustion of the coal at the expense of the oxygen of litharge, the weight of metal produced indicating the amount of oxygen expended, whence the heating power may be calculated. It is found that 1 pt. of pure carbon produces 34·5 of metallic lead; hence if a sample of fuel produces 25, the heating power is $\frac{25}{34\cdot5}$ of that of carbon, or assuming that 1 lb. of carbon raises 7900 lbs. of water 1°, 1 lb. of the sample of coal is capable of raising 5724 lbs. of water by 1°.

Various tables have been given by Berthier and other experimenters, of results obtained in this manner, the following being some of the most useful figures: —

Coking Dowlais coal	produces	31·8 lbs. lead
Glamorgan	„	31·2 „
Newcastle	„	30·9 „
Wigan cannel	„	28·3 „
Cherry coal, Derbyshire	„	27·2 „
Glasgow cannel	„	24·9 „
Durham	„	31·6 „
Pennsylvanian anthracite	„	30·5 „

By a comparison of the result of any experiment with these standard figures, a tolerably fair estimate may be made of the specific value of any sample.

The method of operating consists simply in mixing a known weight of the finely powdered fuel with about forty times its weight of pure litharge, and exposing the mixture to a gentle heat in a large crucible finally raised to a clear red heat. The pot is removed, struck on the floor to assist the settling of the metal, and broken when cold. The button is cleaned and weighed. The accuracy of the result depends greatly upon the relative proportion of hydrogen and oxygen: when they are in the proportion necessary to form water, the result is tolerably correct; but it is evident that any excess of hydrogen over and above this proportion introduces an error, inasmuch as its heat equivalent is calculated as if it were carbon, while in truth it is about four times as great. The results of the British Admiralty investigation, by De la Beche and Playfair, exhibit a variation often "amounting even to a virtual contradiction" of the simultaneous results of direct combustion.

Other experimenters have found difficulty in obtaining constant results by Berthier's method, but Mitchell has found that the difficulty may be obviated by substituting ordinary carbonate of lead for the litharge.

The best practical method of valuing fuel consists in employing an apparatus similar to those used by Andrews and other chemists in the determination of the actual heating power of carbon, hydrogen, &c., or of a miniature furnace to which a known volume of air is supplied, with arrangements, such as readily suggest themselves, for the complete utilisation of the heat evolved. It is to be remembered that the real value of all such results is simply relative.

The imperfect character of most boiler arrangements and the large quantity of coal which passes into the ash-pit unconsumed, together with the irregular supply of draught and the amount of heat absorbed by the great excess of cold air, result practically in an enormous loss of heating power, to an extent which, even under the most careful management, is widely variable. Thus, the results obtained in the American and British Admiralty experiments exhibit grave discrepancies. In the case of the latter investigation, a Cornish boiler only 12 feet long was employed, and "even from the smallness of the boiler employed, the results fell short by 20 per cent. of the maximum amount of work which the same fuels could perform when applied to larger boilers constructed and set on the same principle. The inquiry is rendered less efficient from another cause, viz. the want of a thorough control and measurement of the air passing through the furnace."

We have referred to the injurious properties of *sulphur* as an ingredient in coals, and to its average quantity in various classes of fuel. Its amount may be estimated by fusing in a large silver capsule a few pieces of caustic potash and ⅓ of its weight of nitrate of potash and a few drops of water. After cooling, the finely powdered coal is added, and the whole re-fused till white. The mass is dissolved in hydrochloric acid, and the sulphuric acid produced is estimated by precipitation with chloride of barium. It is always necessary at the same time to estimate the quantity of sulphuric acid present in the ash of the coal, and to deduct this from the amount obtained as above, in order to obtain the quantity due to the oxidation of the sulphur only.

Deflagration with 2 pts. nitre and 10 of chloride of sodium may also be employed, but the greatest care is necessary to control the action.

The importance, in addition to a knowledge of the chemical character of a fuel, of a consideration of its *mechanical condition*, is amply exhibited by the fact acknowledged in both the government series of experiments, that it was a *sine quâ non* that the toughness of coals must be such, for naval use, as to resist, without crumbling, the constant friction in the ship's hold, at the same time that its fracture must be such that it packs into the smallest possible space. In this respect, coals of equal heating power vary 20 per cent. at least. "This factor, which is of extreme importance in steam-navigation, becomes reduced the more the cleavage of the coal or the shape of the fuel approaches the form of a cube. In order to attain, at least, a relative idea of the waste occasioned by transport, *i. e.* of the attrition of the individual pieces of coal against each other, and conversion of unbroken coal into dust unfit for use, which is occasioned by the motion of the vessel, the various specimens were rotated in a drum for the same length of time, and the dust thus produced separated and weighed."

The subjoined table shows some of the results of the British investigation as regards:

1. Number of lbs. of water at 100° C. converted into steam by 1 lb. of fuel.
2. Ditto, after deducting portions of coke contained in the ash.
3. Theoretical evaporative power in lbs. of water of 100° C. evaporated by 1 lb. of fuel calculated from litharge test.
4. Weight of coal per cubic foot of stowage in lbs.
5. Ditto, per solid cubic foot, deduced from specific gravity.
6. Percentage loss by equal amount of attrition.

Kind of Fuel.	1.	2.	3.	4.	5.	6.
Welsh:—						
Jones and Co's Anthracite	9·46	9·70	13·84	58·25	85·79	68·5
Ward's Fiery Vein	9·40	10·60	16·40	57·43	83·85	46·5
Graigola	9·35	9·66	16·72	60·17	81·11	49·3
Duffryn	10·14	11·80	15·64	53·22	82·72	56·2
Ponty Pool	7·47	8·04	14·31	55·70	82·35	57·5
Ebbw Vale	10·21	10·64	16·68	53 30	78·81	45·0
Bedwas	9·79	9·99	14·70	50·50	82·60	54·0
Scotch:—						
Dalkeith Jewel	7·08	7·10	13·77	49 80	79·67	85·7
Wallsend Elgin	8·46	8·67	15·15	54·60	78·61	64·0
Fordel Splint	7·56	7·69	15·12	55·00	78·61	63·0
Grangemouth	7·40	7·91	14·85	54·25	80·48	69·7
English:—						
Broomhill	7·30	7·66	13·20	52·50	77 99	65·7
Park End, Sydney	8·52	8·98		54·44	80·05	55 0
Irish:—						
Slieverdagh	9·85	10·49	16·21	62·80	99·57	74·0
Mean of three patent fuels	9·27	9·66	15·44	66·48	70·66	

For further information on coal, see *Ure's Dictionary of Arts, Manufactures and Mines*, i. 696; also *Ronalds and Richardson's Chemical Technology*, 2nd ed. i. [1] 28; i. [2] 761; *Percy's Metallurgy*, i. 78—106. W. W.

COAL-GAS. The gas produced by the destructive distillation of pit-coal at regulated temperatures.

The apparatus used in the manufacture of coal-gas on the great scale consists essentially of a system of closed retorts of fireclay or cast-iron, the exit pipes from which communicate with a *hydraulic main*, in which the crude gas deposits part of its tar and ammoniacal products. It passes thence into a series of condensing pipes, wherein it is exposed to the action of a large refrigerating surface, and deposits the greater part of its tar and ammonia-liquor, the last portions being removed in its passage through another series of vessels of various forms and modifications, in which the gas is *scrubbed*, by being obliged to force its way through breese, stones, or other materials which serve to comminute it and bring it into thorough contact with a stream of water which continually percolates the vessel. It is then deprived of its carbonic acid and sulphuretted hydrogen in lime purifiers, and finally is drawn by exhausting apparatus into the gas-holders, passing on its way through the station-meter and other beautiful and delicate apparatus, whereby the pressure and amount of gas which passes into the town are regulated and registered. (See the article COAL-GAS in *Ure's Dictionary of Arts, Manufactures and Mines.*)

The following analysis by Bunsen and Roscoe exhibits the composition of Manchester coal-gas prepared from Cannel coal:

Hydrogen	45·58
Marsh-gas	34·90
Carbonic oxide	6·64
Olefiant gas or ethylene	4·08
Tetrylene	2·38
Sulphuretted hydrogen	0·29
Nitrogen	2·46
Carbonic acid	3·67
	100·00

In addition to these constituents, there are frequently present traces of ammonia, vapour of sulphide of carbon, cyanogen, and oxygen.

The composition above given, represents that of a first-rate sample of gas; but the relative proportion of the several ingredients depends both upon the quality of coal used, upon the temperature of the retorts, and the time during which the distillation is continued. It is to the olefiant gas and other heavy hydrocarbons present in comparatively small quantities, that the illuminating power of gas is chiefly due; the maintenance of a full proportion of this gas is therefore of the utmost importance. The following table shows the quality of gas from 1120 lbs. of common coal at the Clifton gas-works, Manchester, at different periods of distillation:

Hours from commencement.	100 measures purified gas contain			100 measures of purified gas consume
	Olefiant gas.	Nitrogen.	Other inferior gases.	Oxygen.
1	10	0	90	164
3	9	0	91	168
5	6	0	94	132
7	5	15	80	120
9	2	9	89	112
11	0	15	85	90

Hence, two things should especially be avoided in the manufacture of gas, viz. too low a heat and a too long continuation of the distillatory process. The effect of too low a heat is a great diminution of the gaseous products, the chief result of the distillation being the production of tar. The effect of continuing the distillation too long, is that gases of very feeble illuminating power are evolved, together with nitrogen, which, when once mingled with the combustible gas, cannot be removed by any known method, and must seriously impair its illuminating power.

The following table by Hughes gives an idea of the relative and absolute yield of different kinds of coal under practical management:

Name of Coal.	Cubic feet of Gas per ton.	Specific Gravity of Gas.	Weight of Gas in lbs. per ton of Coal.	
Newcastle, average of 3 samp.	11,492	·452	398	Hedley.
„ „ 10 „	11,336	·416	362	Clegg.
Wigan cannel	9,500	·490	357	Fyfe.
„	9,408	·478	344	Wright.
Scotch Parrot	9,500	·640	466	„
Lesmahago cannel	11,312	·737	638	Hedley.
Boghead cannel	15,000	·752	866	Evans.
Ince Hall cannel	11,400	·528	461	„
Derbyshire	9,400	·424	308	Wright.
„ soft, aver. of 3 samp.	7,166	·466	256	Parliamentary return.
Neath, South Wales	11,200	·468	401	Hedley
Westbromwich, parliamentary return of Birmingham gas company	6,500	·453	226	
Staffordshire, average of 4 samples	10,467	·376	302	Clegg.

Modes of estimating Luminiferous Value.

The gas manufacturer relies much as an indication of the purity of his gas, upon its specific gravity, which he commonly takes approximately by means of a balloon, containing when full 1000 cubic inches, and gauged by a ring which fits its largest diameter when full. Attached to the balloon is a car, into which as many grains are put as balance the balloon. This result, although not scientifically accurate, gives, after correction for temperature, barometer, &c., an indication of sufficient practical value, but of course vitiated by the presence of any large amount of carbonic acid.

The comparison of gases by the photometer is a test preferred by many gas-engineers to all others. It consists of the comparison either of shadows, or of transmitted light passing through a semi-transparent disc of paper with reflected light striking on an opaque portion, in juxtaposition to the transparent portion. When the light is so adjusted that the shadows are precisely similar, or that the light reflected and that transmitted by the disc are equal, then the lights are to each other in the ratio of the squares of their distance from the disc or screen.

The only chemical test upon which the practical gas maker commonly relies, is the amount of absorption which takes place upon introducing into a known volume of gas a bubble of chlorine or a drop of bromine, the principal hydrocarbons to which gas owes its luminiferous value being condensed by these reagents into oily compounds. These methods are, however, of the roughest kind.

An accurate result may, however, be obtained by substituting for chlorine or bromine a fragment of coke saturated with Nordhausen sulphuric acid, the experiment being made over mercury and the absorption being allowed to go on for two or three hours. Subsequently the sulphurous acid produced in this action is removed by a ball of binoxide of manganese, and finally aqueous vapour is removed by a ball of caustic potash. The quantity of carbonic acid being also determined, the difference between the two experiments gives the amount of luminiferous hydrocarbons accurately. The value of these, being in proportion to the carbon they contain, is ascertained by exploding portions of gas before and after removal of the hydrocarbons with excess of oxygen, and comparison of the amount of carbonic acid produced in each case respectively. The difference is the amount due to the carbon of the luminiferous constituents. (For details of the mode of analysis of such a mixture, we refer to *Miller's Chemistry*, ii. 661, to *Regnault's Cours Elémentaire*, iv. 73, to *Clegg's Treatise on Coal-gas*, and more particularly, for the most recent and accurate methods of operation, to *Bunsen's Gasometry*, p. 107, to the article ANALYSIS (VOLUMETRIC) OF GASES, in this Dictionary, and to the article COAL-GAS in the new edition of *Ure's Dictionary of Arts, Manufactures and Mines*.)

The Rev. W. R. Bowditch proposes to determine the relative illuminating power of coal-gas, in other words, the proportion of ethylene, propylene, and other heavy hydrocarbons contained in it, by the intensity of the red colour which they impart to woody fibre moistened with sulphuric acid. When rich coal-gas, giving the light of 20 to 25 sperm candles from consumption of 5 ft. per hour, is slowly passed through clean deal sawdust, well moistened with pure sulphuric acid diluted with five or six volumes of water, so that it may not blacken the sawdust, that substance instantly acquires a beautiful pink colour, which gradually deepens to a dark mahogany; with a poor gas, which gives the light of only ten or twelve candles at the same rate of consumption, the coloration is faint at first and deepens very slowly. The differences of coloration are so considerable and constant that they may perhaps be used as a means of determining the illuminating value of the gas. By using a standard acid, the same kind of sawdust, a uniform volume of gas, and the same sized U-tubes, notation of time and depth of colour would give a close approximation to the light-giving value. (Proc. Roy. Soc. xi. 25.)

In addition to the constituents estimated by these operations, it is frequently important to determine sulphuretted hydrogen and bisulphide of carbon. Their presence is well detected by the simple and useful apparatus of Wright, consisting of an arrangement for condensing the products of combustion from a gas-jet, and testing the condensed liquid for sulphuric acid.

Their *amount* may be determined by passing a known volume of gas through, 1st, a solution of caustic potash in water, and, 2nd, a solution of the same reagent in alcohol. The former absorbs sulphuretted hydrogen; the latter the sulphide of carbon, which it converts into xanthate of potassium, which is in turn decomposed by boiling. Dilute solution of nitrate or acetate of lead being added, sulphide of lead is precipitated, and its amount is judged of by comparison of the shade of colour produced in the liquid with a solution containing a known quantity of lead precipitated in the like form.

Another method of detecting sulphide of carbon in coal-gas, is to pass it through an ethereal solution of *triethylphosphine*, which forms with sulphide of carbon a compound crystallising in splendid ruby-red prisms (Hofmann, Chem. Soc. Qu. J. xiii. 87). This is a much more delicate test than the preceding. Hofmann found that, on passing a current of coal-gas through a solution of four or five drops of triethylphosphine in ether contained in a bulb-apparatus, a distinct red coloration was produced after 0·2 of a cubic foot of gas had passed through the liquid; and after 0·8 of a cubic foot had passed, the whole of the ether had evaporated, and the inner surface of the bulb-apparatus was lined with a beautiful net-work of the ruby crystals.

Lastly, the sulphide of carbon may be easily detected by a method which likewise serves for its removal. For this method we are indebted to the Rev. W. R. Bowditch (*loc. cit.*) It consists in decomposing the sulphide of carbon with hydrogen, thereby converting it into sulphide of hydrogen, which is easily detected and removed by the usual methods. When a mixture of hydrogen and vapour of sulphide of carbon is passed through a tube filled with slaked lime or clay, which has been dried between 400° and 500° Fahr., and is kept between 400° and 600° during the passage of the gaseous mixture, the sulphide of carbon is completely decomposed, the lime or clay is blackened by a deposit of carbon, and sulphur sublimes in the exit-tube, while sulphide of hydrogen passes through, and may be detected by acetate of lead. The same effect is produced when coal-gas containing sulphide of carbon is passed over heated lime or clay, the free hydrogen in the gas then decomposing the sulphide of carbon in the manner just described. This method may be applied on the large scale to the purification of coal-gas from sulphide of carbon, the sulphuretted hydrogen resulting from the decomposition being afterwards removed by slaked lime in the ordinary way. Passing the gas over clay likewise decomposes other volatile sulphur-compounds which are not removed by the ordinary mode of purification with lime. These compounds, including sulphide of carbon, have long been regarded as the most troublesome impurities of coal-gas. The sulphur which is evolved from the coal as sulphuretted hydrogen, is easily removed by slaked lime; indeed, the London coal-gas rarely, if ever, exhibits the slightest trace of this compound. But it always contains sulphide of carbon or some of the other volatile sulphur-compounds just mentioned, the proportion of sulphur contained in it varying, according to Hofmann (*loc. cit.*), from 6·68 to 10·33 grains in 100 cubic feet. Now the sulphur in burning produces sulphurous acid, which, besides being offensive to the senses, is very destructive to art-decorations, bindings of books, &c. The removal of these sulphur-compounds will, therefore, do away with the greatest existing objection to the use of gas in dwelling houses.

The use of clay as a purifier of coal-gas is likewise attended with other advantages, as it absorbs ammonia and other nitrogen-compounds which diminish the light-giving power of the gas. This effect is especially conspicuous when the gas given off towards the end of the distillation (p. 1036), is submitted to the action of the clay.

Clay which has become charged with the impurities from coal-gas, may afterwards be used as a manure.

Secondary Products obtained in the manufacture of Coal-gas.

After a charge of coal has been worked off to the extent considered most desirable, the man-lids are removed from the retorts, and the residual coke raked out into barrows, wheeled away and quenched with a jet of water. Its appearance and uses, as fuel for locomotives, in the blast furnace, and in a vast number of technical operations, are too well known to need description, nor does space allow us to go into details of the numerous processes which have been employed, with more or less success, for the economical preparation and purification of coke.

The liquids condensed during the passage of the gas through the hydraulic mains and condensers, are of a very complex character. They consist essentially of two portions, the one watery and the other tarry, crude coal-tar varying in density between 1120 and 1150, the lightest portions containing the largest proportion of liquid oils.

The basic substances contained in coal-tar include ammonia, aniline, picoline, chinoline, pyridine, toluidine, and others of less importance.

The acids include acetic in minute quantities, rosolic, brunolic, &c., but principally phenic or carbolic acid. The neutral portions contain benzene, toluene, cumene, cymene (liquids); naphthalene, paranaphthalene or anthracene, chrysene, and pyrene (solids).

The commercial distillation of coal-tar is performed in large retorts, holding from 200 to 500 gallons. The first products are gaseous; next passes water charged with ammoniacal salts, and contaminated with black oily matter.

The proportion of oil continues to increase, while that of watery products diminishes. Finally, after from 5 to 10 per cent. of the whole has passed in the form of "light oil," the product becomes heavier than water, and is collected apart as "kreasote oil," or "dead oil" used extensively for the pickling or antiseptic preparation of timber, and for burning into lamp-black. Naphthalene and other solid products now become abundant and the oil becomes pasty. Finally, the residue in the retort is run off while hot, and on cooling becomes hard and brittle, constituting *asphalt*, a product used in the manufacture of coarse varnishes, and on a vastly larger scale in laying down railway and other bridges, as a means of protecting their masonry from the infiltration of water.

The heavy oil contains a variety of hydrocarbons of high boiling point, together with carbolic acid, to which latter it probably owes its antiseptic qualities.

The light oils obtained in the above process are rectified, whereby a further portion of heavy oils is separated and crude *naphtha* obtained. This is agitated with sulphuric acid. and the supernatant liquid, upon careful rectification, yields the "highly rectified naphtha" or "benzole" of commerce, consisting of a complex mixture of at least five oils boiling at from 149° to 392° F., and of specific gravity ·860 to ·890.

The watery liquids deposited in the condenser during the manufacture of gas, are devoted to the production of sulphate and chloride of ammonium. They are usually removed from the gas-works in flats or canal boats of known capacity, under contracts commonly taken at so much per 10,000 gallons.

The manufacture of chloride of ammonium direct from the liquors, is conducted on a large scale in Liverpool, and consists essentially in saturating with hydrochloric acid, concentrating the liquors, crystallising and subsequently subliming the crystals. A far larger portion, however, of the crude gas-liquor is consumed in the manufacture of sulphate of ammonium, by processes which consist essentially of distillation, with addition of lime, to decompose ammoniacal salts, and condensation of the vapour in sulphuric acid, concentration and crystallisation of the solution after saturation has been effected. Sulphate of ammonium is employed in large quantities in the manufacture of artificial manures.

The above are the chief products of distillation of coal at high temperatures, while those at regulated low temperatures are far different. Under the latter conditions, the gaseous products are reduced to their minimum, while the quantity of liquid and solid hydrocarbons is proportionately increased.

The Boghead Cannel of Bathgate, near Edinburgh, is extensively submitted to the process of slow destructive distillation, under the patent of Young, while successful efforts have lately been made by Mr. Blackwell, of Dudley, to turn to account the vast heaps of somewhat bituminiferous shales or "batts" ejected from the coal mines of Staffordshire.

To this subject we cannot further refer than to remark that for practical purposes the products may be separated into three portions.

1. Remains liquid at all ordinary temperatures and forms, after proper purification, a valuable burning oil, known as "photogen."—2. Deposits crystals of solid hydrocarbons at very low temperatures; used extensively for lubricating machinery and known as "paraffin oil."—3. Solid or semi-solid products, which when freed from the oils which contaminate them by pressure, &c. consist chiefly of paraffin (*q. v.*) and may be employed alone or mixed with tallow, stearin, &c. in the manufacture of candles.

W. W.

COBALT. *Kobalt, Cobaltum.—Symbol*, Co. *Atomic Weight*, 29·5.—The use of cobalt for imparting a blue colour to glass, appears to have been known to the Greeks and Romans, though most of their blue glasses were coloured with copper. Some of the pigments used by the ancient Greeks likewise contained cobalt. The use of cobalt for the preparation of smalt was introduced about the middle of the sixteenth century. The metal, in an impure state, was first extracted by Brandt in 1733.

Cobalt is not a very abundant metal. It occurs as an arsenide, called *tin-white cobalt* or *smaltine;* as sulpharsenate, or *cobalt-glance;* as arsenate, or *cobalt-bloom;* as sulphate and as *black earthy cobalt*, which is a compound of protoxide of cobalt with peroxide of manganese. It also occurs in small quantity in other minerals—as in selenide of lead, cerite, and Flemish coal. In the metallic state, it occurs only in meteorites, many of which contain from 0·1 to 1 per cent. of it, associated with iron and nickel.

Preparation.—Cobalt is extracted chiefly from smaltine and cobalt-glance, or from the impure arsenate obtained by roasting these ores. The roasting has the effect of driving off a considerable portion of the arsenic, which escapes as arsenious oxide, and is condensed in the manner described under ARSENIC (i. 365). The roasted product consists essentially of basic arsenite, arsenate and sulphate of cobalt, together with iron, nickel, and in smaller quantity bismuth, tin, copper, and manganese. When prepared on the large scale, it is mixed with twice its weight of siliceous sand, and sent into the market under the name of *zaffre*, which is used for giving a blue colour to glass, enamels, and pottery glaze.

The preparation of a pure oxide of cobalt from the native minerals or the roasted ore, is effected by one of the following processes:

1. Cobalt or smaltine is dissolved in nitric acid, or in dilute sulphuric or hydrochloric acid, to which a little nitric acid is added,—or the roasted ore or earthy cobalt is dissolved in sulphuric or hydrochloric acid alone; the filtered solution is

evaporated nearly to dryness, a large quantity of arsenious acid then separating out; and the liquid is largely diluted, separated from the arsenious acid, and treated with sulphuretted hydrogen as long as the sulphides of arsenic, copper, and bismuth (together with tin) continue to be precipitated. The solution is then filtered, and heated till the excess of sulphuretted hydrogen is expelled and the protoxide of iron converted into sesquioxide; carbonate of sodium is then added in excess, while the liquor is hot, to precipitate the nickel and cobalt in the form of carbonates, and the iron as sesquioxide. The precipitate is then well washed and digested with excess of aqueous oxalic acid; the soluble ferric oxalate is separated by filtration from the oxalates of nickel and cobalt, which are insoluble even in excess of oxalic acid; and the latter salts are triturated with dilute ammonia (it should be strong ammonia according to Stromeyer) and dissolved in excess of the ammonia, by agitation and gentle heating in a close vessel. The filtered solution, after exposure to the air for several days, deposits the oxide of nickel in combination with oxalic acid and a small quantity of ammonia, while pure oxalate of cobalt remains in solution. (The oxalate of nickel separated as above may be freed from the small quantity of cobalt-salt which falls down with it, by washing with water, re-dissolving in ammonia, exposing the liquid to the air, and separating the solution which contains the cobalt from the nickel precipitate, the purity of which increases at each repetition of the process.) The residue obtained by evaporating the ammoniacal solution of the oxalate, yields sesquioxide of cobalt when ignited in the air, and metallic cobalt if ignited out of contact of air. (**Laugier.**)

2. To avoid the tedious passing of sulphuretted hydrogen through the liquid, the arsenic acid may be precipitated by first mixing the dilute solution with a ferric salt, and then adding carbonate of potassium in small successive portions and with constant agitation, as long as the precipitate continues to exhibit a white or brownish colour (arsenate of ferric oxide); till, in short, a filtered sample of the liquid gives a reddish precipitate with a small quantity of carbonate of potassium. If the quantity of ferric oxide be sufficient, and the proportion of carbonate of potassium rightly adjusted, the whole of the arsenic acid and ferric oxide may be precipitated. If the copper and bismuth be then removed by sulphuretted hydrogen, it only remains to separate the nickel from the cobalt. (Berthier.)

3. Finely powdered cobalt-ore is carefully roasted, and 1 pt. of it added in successive small portions to 3 pts. of acid sulphate of potassium heated to the melting point in an earthen or cast-iron crucible. The mass, which is thereby rendered pasty, is then more strongly heated till it fuses quietly and no longer gives off fumes of sulphuric acid, as it is necessary to drive away the excess of that acid. The mass, while yet liquid, is then taken out of the crucible with an iron spoon — broken to pieces after cooling — dissolved in boiling water, and filtered from the arsenates of iron and cobalt, which are not soluble in a neutral liquid. Sulphuretted hydrogen is then passed through the filtrate to throw down any antimony, bismuth, or copper that may be present — the liquid again filtered, and pure carbonate of cobalt precipitated by carbonate of potassium. To prevent the formation of arsenate of cobalt, the roasted cobalt-ore, before fusion with sulphate of potassium, may be mixed with a small quantity of ferrous sulphate, so that the arsenic acid may combine with the oxide of iron contained in that salt in preference to the oxide of cobalt. No nickel is taken up by the liquid, because the sulphate of nickel is decomposed at a red heat [not so, however, the sulphate of nickel and potassium, unless the heat applied is very strong]. The solution retains but a trace of iron at the utmost. (Liebig, Pogg. Ann. xviii, 164.)

4. One part of pulverised smaltine or cobalt-glance is fused in a covered earthen crucible with 3 pts. of carbonate of potassium and 3 pts. of sulphur, whereby the whole of the metals present are converted into sulphides, and sulphide of potassium is formed, which unites with the sulphide of arsenic, forming a soluble sulpharsenate. The heat must be so regulated that the sulphide of cobalt may not fuse, but remain in the form of a crystalline powder, because, if fusion takes place, portions of the sulpharsenate of potassium will be enclosed in the fused mass, and will be difficult to wash out. The mass is then freed from sulpharsenate of potassium by repeated exhaustion with water and decantation; again treated with carbonate of potassium and sulphur, and then with water to remove the rest of the arsenic; afterwards dissolved in nitric acid or in dilute sulphuric acid mixed with nitric; the solution is treated with sulphuretted hydrogen to remove any remaining arsenic, together with bismuth and copper; and the filtered liquid is treated as in method *b*, to separate the cobalt from nickel and iron. (Wöhler, Pogg. Ann. vi. 277.)

5. To obtain cobalt from black earthy cobalt ore, the mineral is dissolved in hydrochloric acid; the arsenic, antimony, lead, and copper are precipitated by sulphuretted hydrogen; the filtrate is boiled with nitric acid to promote the further oxidation of the iron; the iron is precipitated by boiling with acetate of sodium, and the cobalt separated from the filtrate by sulphuretted hydrogen, which leaves acetate of manga-

nese undecomposed. The precipitate is free from nickel, but contains a trace of zinc. The liquid freed from arsenic and copper by sulphuretted hydrogen may likewise be precipitated by sulphide of potassium or barium, and the washed precipitate treated with cold dilute hydrochloric acid, which dissolves the sulphides of manganese, zinc, and iron, and leaves all the sulphide of cobalt undissolved. (Wackenroder, N. Br. Arch. xvi. 133.)

The greatest difficulty in the preparation of pure cobalt-compounds is the separation of the nickel. Laugier's method (*vid. sup.*), affords the means of obtaining a cobalt solution free from nickel; but it leaves a certain portion of the cobalt in the nickel precipitate. For more complete modes of separation, adapted to quantitative analysis, see COBALT, DETECTION AND ESTIMATION OF (p. 1046).

Metallic Cobalt.—Cobalt is reduced from its oxides by ignition with charcoal more easily than iron, or the difficultly fusible brittle metals; when thus reduced, however, it contains carbon. The purest metal is obtained by igniting the oxalate in a covered crucible, the salt, $Co^2C^2O^4$, being then resolved into 2 at. cobalt and 2 at. carbonic anhydride. If the oxalate or the mixture of oxide and charcoal be covered with pounded glass free from reducible metals, and heated in a blast-furnace, the cobalt is obtained in the form of a fused regulus. Cobalt may also be reduced from its oxides by hydrogen; and if the heat applied be not very great, the reduced metal is pyrophoric, like iron reduced under similar circumstances, and takes fire on coming in contact with the air, producing cobaltoso-cobaltic oxide.

Cobalt rendered compact by fusion is rather hard, has a granular fracture, and is somewhat malleable at a red heat. The presence of arsenic, manganese, &c., renders it brittle. It has a steel-grey colour, inclining to red; in the polished state, however, rather to white. The statements respecting its specific gravity vary from 8·513, (Berzelius), to 8·7 (Lampadius). That of the metal reduced by hydrogen was found by Rammelsberg, in five experiments, to vary from 8·132 to 9·495; mean 8·957. Specific heat = 0·10696 (Regnault), 0·1172 (De la Rive and Marcet). It fuses more easily than iron, less easily than gold. It is attracted by the magnet, and is capable of receiving a slight magnetic power when rubbed with a magnet, this power, according to Pouillet, not being destroyed by the strongest red heat. A minute quantity of arsenic destroys the magnetic power.

Cobalt is not altered by the action of air and water at ordinary temperatures, but when very strongly heated, it takes fire, and is converted into cobaltoso-cobaltic oxide, $C^{12}O^7$. It decomposes aqueous vapour at a red heat. It is dissolved by hydracids and by dilute oxygen acids, with evolution of hydrogen, slowly however, and only when heated. The solutions have a fine red colour, and contain salts corresponding in composition to the protoxide. It is easily dissolved by nitric acid, likewise forming a proto-salt.

Cobalt forms several classes of compounds, the most numerous, and generally speaking the best defined being the proto-compounds or cobaltous compounds, *e.g.* CoCl, Co^2O, Co^2S, Co^2SO^4, &c.; there are likewise cobaltic- or sesqui-compounds, *e.g.* Co^4O^3, Co^4S^3; three oxides intermediate between the two preceding; a dioxide, Co^2O^2, a disulphide, Co^2S^2, a tricobaltic phosphide, Co^3P, and several classes of salts containing bases in which cobalt is united with the elements of ammonia.

COBALT, ALLOYS OF. Cobalt unites readily by fusion with antimony and arsenic, the combination being attended with incandescence; the resulting alloys are brittle, and have an iron-grey colour.

Protoarsenide of Cobalt, CoAs, is found native as smaltine or tin-white cobalt, being in fact the most abundant of cobalt ores. It occurs in crystals belonging to the regular system, viz. cubes, octahedrons, dodecahedrons, and intermediate forms. Cleavage octahedral, distinct; cubic, in traces. It occurs also massive and in reticulated and other imitative shapes. Specific gravity 6·3 to 6·6. Hardness 5·5. Lustre metallic. Colour tin-white, inclining sometimes to steel-grey, sometimes to silver-white. It tarnishes by exposure. Streak greyish-black. Brittle. Emits a smell of arsenic when broken. It yields no sublimate when heated in a test-tube; but in a tube open at both ends a sublimate of arsenious acid is formed. It dissolves in nitric acid, leaving a residue of arsenious acid.

Arsenide of cobalt is never found quite pure, the cobalt being always more or less replaced by nickel or iron; those varieties which contain more nickel than cobalt are called *Cloanthite* (see NICKEL). The following are analyses of smaltine containing little or no nickel; *a*, from Riechelsdorf in Hesse, by Stromeyer (Gött. gelehrte Anzeige, 1817, p. 72); *b*, from Tunaberg in Sweden, by Varrentrapp (Pogg. Ann. xlviii. 505); *c*, from Schneeberg in Saxony, by E. Hofmann (*ibid.* xxv. 485); *d*, from the same locality, by v. Kobell; *e*, from Riechelsdorff, by Jäckel (*Rammelsberg's Mineralchemie*, p. 23):—

	As	Co	Fe	Cu	Ni	Bi	S	
a .	74·21	20·31	3·42	0·16	—	—	0·88 =	98·98
b .	69·46	23·44	4·95	—	—	—	0·90 =	98·75
c .	70·37	13·95	11·71	1·39	1·79	0·01	0·66 =	99·88
d .	71·08	9·44	18·48	trace	—	1·00	trace =	99·92
e .	66·02	21·21	11·60	1·90	—	0·04	0·49 =	101·26

The formula CoAs requires 71·8 As and 28·2 Co. When the proportion of iron is considerable, as in *c*, *d*, *e*, the mineral is also called *Safflorite*. The composition of *e* agrees more nearly with the formula $(Co; Fe)^4As^3$. *Chathamite*, from Chatham in Connecticut, is chiefly an arsenide of nickel and iron containing 1·3 per cent. cobalt.

Smaltine occurs altered to cobalt-bloom by oxidation.

Sesquiarsenide of Cobalt. Co^2As^3.—This compound also occurs native as Skutterudite or Modumite (*Tesseralkies*, *Hartkobaltkies*, *Hartkobalt*), at Skutterud, near Modum in Norway. It crystallises in the regular system, exhibiting faces of the cube, octahedron, dodecahedron, and trapezohedron. Cleavage cubic, distinct; dodecahedral in traces. Also massive, granular. Specific gravity 6·74—6·84. Hardness = 6. Lustre bright metallic. Colour between tin-white and pale grey, sometimes iridescent. A crystallised specimen analysed by Wöhler (Pogg. Ann. xliii. 591), gave 79·2 As, 18·5 Co, 1·3 Fe = 99·0, the formula requiring 78·2 per cent. As and 20·8 Co. This mineral heated in a closed tube yields a sublimate of metallic arsenic.

When smaltine is ignited in a retort, part of the arsenic is expelled, and there remains a lower arsenide of cobalt, which is non-magnetic, and fuses before the blowpipe to a brittle metallic globule. In cobalt-blue works, crystallised alloys of cobalt and arsenic are often formed, containing also copper and iron. (Scheerer and Francis, Pogg. Ann. l. 513.)

With $\frac{1}{15}$ of its weight of gold, cobalt forms, according to Hatchett, a dark yellow very brittle compound; even $\frac{1}{65}$ pt. of cobalt is sufficient to render gold brittle.

The alloy of cobalt with iron is very hard and difficult to pulverise.

With mercury, cobalt forms a silver-white amalgam, which is attracted by the magnet.

With platinum, it forms a fusible compound.

When cobalt is fused with silver, two layers are formed, the lower consisting of cobaltiferous silver, the upper of argentiferous cobalt; a small quantity of cobalt renders silver brittle.

With tin, cobalt forms a somewhat ductile alloy of light violet colour.

With zinc, it unites only with great difficulty, also with lead and bismuth, which exhibit with cobalt the same deportment as silver.

COBALT, BROMIDE OF. CoBr.—Cobalt takes up bromine-vapour at a dull red heat, forming a green compound which melts, and at a higher temperature suffers partial decomposition. The compound deliquesces rapidly in the air, forming a red liquid. The same solution is obtained by heating finely divided cobalt with bromine and water. It turns violet-red on evaporation, and leaves a green mass when evaporated to dryness. By evaporating the solution over oil of vitriol, red crystals of the hydrated bromide acid are obtained, which soon effloresce in the dry air of the receiver, but deliquesce when exposed to the air in its ordinary state. (Rammelsberg.)

A solution of the bromide forms, with excess of *ammonia*, a blue precipitate, which turns green on exposure to the air, and a red solution which turns brown in the air, and then sometimes deposits red quadratic tables, perhaps consisting of a compound of Co^2Br^3 with bromide of ammonium. (Rammelsberg.)

Bromide of cobalt absorbs *ammonia-gas*, forming ammonio-bromide of cobalt, $3NH^3.CoBr$, a red powder which gradually turns brown, and is resolved by water into a brown solution, and an insoluble green residue containing bromine. (Rammelsberg.)

COBALT, CHLORIDES OF. The *protochloride*, CoCl, is formed, with vivid incandescence, when pulverulent cobalt is heated in a stream of chlorine-gas; it then sublimes in blue crystalline scales. It is also produced in the wet way by dissolving cobalt or the protoxide in hydrochloric acid, hydrogen being evolved in the former case, or by heating the sesquioxide or cobaltoso-cobaltic oxide (Co^3O^4), with hydrochloric acid, its formation being then attended with evolution of chlorine. The solution is pink, and yields by evaporation non-deliquescent crystals of the same colour, consisting of hydrated chloride of cobalt. But if the pink solution be mixed with strong hydrochloric or sulphuric acid, it turns blue the more readily as it is more concentrated and more strongly heated. The effect appears to be due to the abstraction of the crystallisation-water by the strong acid. According to Proust, such a solution sometimes deposits the blue crystals of the anhydrous chloride. The red colour is restored by dilution with water. By evaporating the solution to dryness, or by heating the hydrated crystals, hydrochloric acid is evolved, and a greenish blue mass is obtained, consisting of an oxychloride (Berzelius), which is decomposed at a higher temperature, yielding a sublimate of anhydrous chloride, and leaving an oxidised compound.

The sublimed chloride forms soft loose crystalline spangles, unctuous to the touch, and of light blue colour. On exposure to the air, it takes up water and becomes rose-red, and is then easily dissolved by water, forming a red solution; but if not previously hydrated in this manner, it is very slowly dissolved by water.

The red solution forms a sympathetic ink. Characters written with it on paper are colourless and invisible or nearly so; but when the paper is warmed by holding it near a fire, the writing becomes visible and appears of a beautiful blue. After a while, as the salt absorbs moisture, the colour disappears, but may be reproduced by the action of heat. If the paper be exposed to too high a temperature, the writing becomes black, and does not afterwards disappear. The addition of a nickel-salt to the solution gives a green instead of a blue colour.

Ammonio-chloride of Cobalt, $2NH^3.CoCl$, obtained by passing ammonia-gas over the heated chloride, is a bulky powder of a pale reddish-white colour. With water it forms a red-brown solution, and leaves a green powder. (H. Rose.)

Sesquichloride of Cobalt, Co^2Cl^3, is a very unstable compound, formed by dissolving hydrated cobaltic oxide in cold hydrochloric acid. A brown solution is thus obtained, which begins to evolve chlorine, and pass into the protochloride, this effect taking place instantly on heating the liquid. The sesquichloride is also formed in small quantity when chlorine is passed through a solution of the protochloride mixed with hydrochloric acid, the liquid then assuming a darker colour.

COBALT, DETECTION AND ESTIMATION OF. 1. *Blowpipe Reactions.*—All compounds of cobalt fused with borax or phosphorus-salt before the blowpipe, either in the inner or the outer flame, impart a splendid blue colour to the bead, affording an extremely delicate test of the presence of the metal. The production of the blue colour in *both* flames distinguishes cobalt from all other metals. If the substance under examination contains a large quantity of manganese or iron, as well as cobalt, the bead formed in the outer flame is violet in the former case, green in the latter. If the glass be then heated in the reducing flame, the manganese colour disappears, and that of iron changes to bottle green, the glass then exhibiting either the pure blue due to cobalt, or the greenish blue of a mixture of cobalt and iron.

Cobalt-salts mixed with carbonate of sodium, are reduced on charcoal to a grey magnetic powder of metallic cobalt.

2. *Reactions in Solution.*—Solutions of proto-salts of cobalt or cobaltous salts have a rose-red colour, excepting when they are very concentrated and contain a free acid, in which case they are blue; dilution with water changes the blue colour to red (p. 1042). The neutral solutions faintly redden litmus. *Sulphydric acid* produces no precipitate in cobalt solutions containing an excess of either of the stronger acids; but in a solution of the acetate, or of any cobalt-salt mixed with acetate of potassium it forms a black precipitate of sulphide of cobalt. *Alkaline sulphides* throw down the same precipitate, insoluble in excess of the reagent.

Potash or *soda* forms in cobaltous solutions a blue precipitate of a basic salt, which is insoluble in excess of the reagent, assumes a green or dirty bluish-grey colour on exposure to the air, from formation of sesquioxide, but if protected from the air, is converted into the hydrated protoxide of a dingy red colour. This last change takes place quickly on heating the liquid, even if the air be not excluded. A solution of protochloride of cobalt containing a little sesquichloride, yields with potash a precipitate which does not change to dingy red, even on boiling, but merely acquires a darker colour.

Ammonia added in small quantity to a cobaltous solution forms a blue precipitate consisting of a basic salt, which, by continued digestion with ammonia out of contact of air, is converted into rose-red hydrated cobaltous oxide, the change being, however, much slower than when a fixed alkali is used as the precipitant. In contact with the air, the precipitate becomes green. If more ammonia be added, it dissolves and forms a brownish-red liquid, which, if exposed to the air, absorbs oxygen, becomes red-brown, and then contains salts of various bases, consisting of the elements of ammonia united with the higher oxides of cobalt (see Cobalt-Bases, Ammoniacal). If the solution contains but a small quantity of ammoniacal salts, which will be the case if the original cobalt solution was neutral, potash produces in it a precipitate of hydrated sesquioxide of cobalt; but if chloride of ammonium be added, or if the original solution contained an excess of acid which has been neutralised by the ammonia, potash produces no precipitate.

Neutral *carbonate of potassium* or *sodium*, forms a rose-coloured precipitate of hydrocarbonate of cobalt, which, when boiled, gives off carbonic acid, and assumes a violet, or, if the alkaline carbonate is in excess, a blue colour. If the precipitate be boiled for some time in contact with the air, its colour changes to green. A solution of *acid carbonate of potassium* forms, in neutral cobaltous solutions, a rose-coloured precipitate, with evolution of carbonic acid, the liquid retaining a reddish colour which it does not lose for a very long time. The precipitate ultimately changes to a mass of small rose-coloured crystals, consisting of a compound of neutral carbonate of cobalt with acid carbonate of potassium. Frequently, also, there is formed a compact precipitate, destitute of crystalline structure, and consisting of a compound of neutral carbonate of cobalt with a very small quantity of cobaltous hydrate.—*Carbonate of ammonium* produces a red precipitate of carbonate of cobalt, soluble in excess of the precipitant and in chloride of ammonium; the solution does not turn brown in contact with the air.

Carbonate of barium does not in general precipitate cobaltous salts at ordinary temperatures; from a solution of the sulphate, however, the greater part of the cobalt is precipitated after a very long time, so that the remaining liquid is nearly colourless. From a solution of the chloride, no precipitation takes place in the cold, but by prolonged boiling, the whole of the cobalt is precipitated.

Oxalic acid produces, after some time, a faintly reddish white precipitate, which gradually increases, the whole of the cobalt being ultimately thrown down as oxalate. The precipitate is soluble in ammonia, less easily in carbonate of ammonium. The rose-coloured ammoniacal solution, when exposed to the air, very slowly deposits the oxalate.

Phosphate of sodium produces in neutral cobaltous solutions, a blue precipitate of cobaltous phosphate, soluble with red colour in excess of the cobalt-solution, deposited again on boiling, and redissolving as the liquid cools.

Cyanide of potassium produces a red-brown precipitate completely soluble in excess. The solution has a grass-green colour, changing, after a while, to pale brown, and yields, with hydrochloric acid, a reddish-white precipitate, soluble in potash. Sulphide of ammonium does not precipitate the cobalt from this solution, even after a long time.

Ferrocyanide of potassium produces a green precipitate of ferrocyanide of cobalt, changing after a while to grey; insoluble in hydrochloric acid. *Ferricyanide* of potassium produces a reddish-brown precipitate, likewise insoluble in hydrochloric acid.

Brown peroxide of lead mixed with the solution of a cobaltous salt, precipitates nearly all the cobalt, after some time, in the form of sesquioxide; the reaction is accelerated by heat.

The non-precipitation by sulphydric acid in presence of free mineral acids, and the reactions with alkalis,—especially the formation of a brownish-red solution with excess of ammonia, from which sulphide of ammonium throws down a black precipitate,—are together sufficient to distinguish cobaltous solutions from all others. The blowpipe reaction will of course be resorted to as a confirmatory test.

Many non-volatile organic substances, such as tartaric acid, prevent the precipitation of cobalt by alkalis, but not by sulphide of ammonium.

Sesqui-salts of cobalt, or cobaltic salts.—The liquid formed by passing chlorine into a solution of a cobaltous salt, or by treating it with chlorate of potassium and hydrochloric acid, till it assumes a brown-red colour and smells strongly of chlorine, exhibits the following reactions:—

Sulphydric acid produces no precipitate, but only a milkiness arising from separation of sulphur, the solution at the same time acquiring the rose-red colour characteristic of cobaltous salts. *Sulphide of ammonium*, after saturation of the free acid by ammonium, produces a black precipitate of sulphide of cobalt. *Potash*, a dark black-brown precipitate of hydrated cobaltic oxide. *Ammonia*, a brownish-red solution, which does not change by contact with the air. *Carbonates of potassium and sodium:* green solution which deposits a small quantity of sesquioxide. *Ferrocyanide of potassium*, a green; and *ferricyanide of potassium*, a brownish-red precipitate. *Oxalic acid* slowly produces a precipitate of cobaltous oxalate.

3. *Quantitative estimation.*—Cobalt is generally precipitated from its solutions by *caustic potash*. The basic salt at first thrown down is converted into hydrate (p. 37) by boiling in the liquid, and then well washed with hot water to free it from alkali, which adheres very obstinately to it. It is then dried and ignited in an atmosphere of hydrogen, by which it is reduced to the metallic state. The reduction is most easily performed by placing the dried precipitate in a platinum or porcelain crucible, through the lid of which passes a tube connected with a hydrogen apparatus. The crucible must be heated to full redness over a lamp; if a lower degree of heat be applied, the reduced cobalt will be pyrophoric, and is sure to oxidise partially during weighing. The stream of hydrogen must be kept up till the crucible is quite cold.

As the precipitate thrown down by potash almost always retains a small quantity of alkali, even after prolonged washing, the reduced metal must, after weighing, be well washed with water, till the liquid which runs away no longer exhibits any alkaline reaction. The metal is then to be dried, again ignited in hydrogen gas, and weighed. The difference between the two weighings seldom exceeds 0·2 per cent. If the cobalt has been precipitated from a solution of the sulphate, the precipitate may retain a small quantity of sulphuric acid: in that case, the reduced metal will contain sulphur, but never more than a mere trace, unless the precipitate has been boiled with the liquid for a very long time.

Alkaline carbonates do not precipitate cobalt so completely as the caustic alkalis.

If the cobalt-solution contains ammoniacal salts, the precipitation is not complete even when a caustic alkali is used, and the liquid well boiled. In that case it is necessary to precipitate by *sulphide of ammonium*, wash the precipitate, dry it on the filter, burn the filter to ashes, then dissolve the sulphide in nitric or nitromuriatic acid, and precipitate with potash as above.

If the solution contains none but easily volatile acids, such as nitric or hydrochloric acid, and no fixed base but cobalt, the precipitation may be dispensed with altogether, the liquid being merely evaporated to dryness in the crucible, and the residue ignited in an atmosphere of hydrogen, in the manner already described.

Lastly, cobalt may be completely precipitated from its neutral solutions by *nitrite of potassium*, in the form of potassio-cobaltic nitrite, or cobalt-yellow (p. 1058). The solution is evaporated to a small bulk, and neutralised by potash if it contains excess of acid. A solution of nitrite of potassium is then added, together with sufficient acetic acid to neutralise any free potash in the nitrite: the whole is left at rest for two days, and the yellow compound which has separated is collected on a filter. The filtered liquid should also be treated with nitrite of potassium and acetic acid, and left at rest for some time, in order to see whether any further precipitate forms. The precipitate is washed with solution of chloride or sulphate of potassium, then dissolved in hydrochloric acid, the liquid being heated till it is quite free from nitrous acid, and exhibits the rose-red colour of a cobaltous salt, and the cobalt is finally precipitated by potash. This mode of precipitation serves to separate cobalt from nickel, zinc, manganese, and many other metals. (A. Stromeyer, Ann. Ch. Pharm. xcvi. 218.)

4. *Separation from other elements.*—The metals of the first group (i. 217), are separated from cobalt by precipitating them with *sulphydric acid*, from solutions acidulated with one of the stronger mineral acids. From the metals of the third group and from the non-metallic elements, cobalt is separated by precipitating it as a sulphide with *sulphide of ammonium* from neutral or alkaline solutions. In applying this method to the separation of cobalt from magnesium, it is necessary to add chloride of ammonium to retain the magnesia in solution, and even then the sulphide of cobalt sometimes carries down with it a small quantity of magnesia. This may, however, be prevented by boiling the whole till the free ammonia present is volatilised, then adding a few drops of sulphide of ammonium, and filtering.

Aluminium is best separated from cobalt by precipitation as insoluble diacetate (i. 13). The solution, if acid, is neutralised with carbonate of sodium, *acetate of sodium* is added, and the liquid boiled for some time. The alumina is then precipitated in a form in which it may be easily filtered and washed. The washing must be performed with a warm weak solution of acetate of sodium, as the precipitate is slowly dissolved by pure water. The whole of the cobalt remains in solution, and the alumina, which may contain soda, is dissolved by hydrochloric acid, and precipitated by sulphide of ammonium (i. 155). (H. Rose.)

Aluminium cannot be separated from cobalt by *solution of potash*, the precipitated oxide of cobalt always carrying some of the alumina with it. A better method is to fuse the mixture of the two bases with solid potash in a silver crucible, and extract the fused mass with water. The oxide of cobalt which then remains may contain a little potash, but it is free from alumina.

Another very good mode of separation is to mix the solution of the two bases with tartaric acid and excess of ammonia,—which will not then precipitate either of them,—and add sulphide of ammonium, which will throw down the cobalt and leave the aluminium in solution. The precipitated sulphide of cobalt is then to be treated with nitric acid, &c., as already explained; the filtrate containing the alumina evaporated to dryness, and the residue ignited to burn away the organic matter. If no other base is present, the ignited residue will consist of pure alumina, which may be weighed; in the contrary case, the residue must be dissolved in hydrochloric acid, and the alumina precipitated by one of the methods given on page 155, vol. i. As the burning away of the organic matter takes a long time, it is perhaps better to destroy it by boiling the liquid with chlorate of potassium and hydrochloric acid, and then precipitate the alumina.

Cobalt may also be separated from aluminium by precipitation with *nitrite of potassium*.

From **glucinum**, cobalt may be separated by either of the two methods last-mentioned; also from **yttrium**, **zirconium**, **thorium**, **cerium**, **lanthanum** and **didymium**. The last three metals may also be separated from cobalt by precipitation with *sulphate of potassium* (i. 833), or with oxalic acid from a solution containing excess of ammonia.

From **iron**, cobalt is most easily separated by precipitating the two metals with *sulphide of ammonium*, and digesting the washed precipitate in dilute hydrochloric acid, which dissolves the iron and leaves the cobalt. As, however, very small quantities of sulphide of cobalt may likewise be dissolved, it is best to reprecipitate the iron by sulphide of ammonium, and treat the precipitate with very dilute hydrochloric acid: any slight traces of cobalt that may be mixed with the iron will then be left undissolved.

Cobalt may also be separated from iron (in the state of sesquioxide) in the same manner as aluminium, viz. by boiling the neutralised solution with *acetate of sodium*. The iron is then precipitated, while the cobalt remains in solution. The iron precipitate is washed with warm dilute acetate of sodium, dissolved in hydrochloric acid, and the iron reprecipitated by ammonia; and the cobalt is precipitated by sulphide of ammonium. If the iron in the original solution is in the state of protoxide, it must first be converted into sesquioxide by heating with nitric acid. This method yields very exact results.

A third method of separating iron (as sesquioxide) from cobalt, is to mix the solution, if neutral, with a considerable quantity of chloride of ammonium, then cautiously add ammonia till a permanent precipitate of ferric oxide just begins to form, and precipitate the rest of the iron with *succinate of ammonium*. The cobalt remains in solution, and the ferric succinate, after being washed and dried, is ignited with good access of air, to prevent reduction of iron by the organic matter (see IRON). This method is not, however, so good as the two preceding, as the oxide of iron, when examined by the blowpipe, always exhibits the presence of a small quantity of cobalt.

Lastly, cobalt may be separated from iron by precipitation with *nitrite of potassium*.

From **manganese** (existing in solution as a manganous salt) cobalt may be easily separated by precipitating the two metals as sulphides, and dissolving out the sulphide of manganese with dilute hydrochloric acid, in the same way as for iron.

Another method, proposed by Liebig, is to precipitate the two metals as cyanides with *cyanide of potassium*, then add a sufficient excess of that reagent to redissolve the cyanide of cobalt and part of the cyanide of manganese. The latter is collected on a filter and washed; the filtered liquid is heated, and hydrochloric acid is slowly added by drops, care being taken not to add enough to render the liquid acid; and the separation of the cobalt and manganese is effected exactly in the manner which will be presently described for the separation of cobalt and nickel. The cyanide of manganese previously separated by filtration is dissolved in hydrochloric acid; the solution is boiled till the hydrocyanic acid is completely volatilised, the manganese is precipitated by carbonate of sodium, and the quantity thus obtained is added to that determined the other way.

If the cobalt and manganese exist in solution as chlorides, the liquid may be evaporated to dryness (being transferred to a porcelain crucible when reduced to a small bulk), and the residual chlorides ignited in an atmosphere of *hydrogen* in the manner described at p. 1043, as long as vapours of hydrochloric acid continue to escape. The cobalt is then reduced to the metallic state, while the chloride of manganese remains undecomposed, and may be dissolved out by water. The metallic cobalt which remains is washed with hot water, then digested with a small quantity of very dilute acetic acid, to dissolve out any small quantity of chloride of manganese that may remain, afterwards ignited in a current of hydrogen, and weighed. The manganese is precipitated from the solution of its chloride by carbonate of sodium. If the temperature be raised too high during the reduction by hydrogen, a small quantity of chloride of manganese may be volatilised.

Another mode of separating cobalt from manganese, is to digest the mixed protoxides (precipitated by an alkali) in a solution of *pentasulphide of calcium*, which converts them both into sulphides, dissolving the sulphide of cobalt, and leaving the sulphide of manganese undissolved.

From **nickel**, as from most other metals of the second group, cobalt is most easily separated by precipitation with *nitrite of potassium*, the process being performed exactly as described at p. 1045. With due attention to the precautions there indicated, the whole of the cobalt is precipitated, without a trace of nickel.

Another method is that of H. Rose, depending on the fact that protoxide of cobalt in solution is converted by *chlorine* into sesquioxide, whereas with nickel this change does not take place. The metals or their oxides being dissolved in excess of hydrochloric acid, the solution is diluted with a large quantity of water, about a pound of water to a gramme of the metals or their oxides. Chlorine gas is then passed through the solution for several hours, till, in fact, the space above the liquid becomes permanently filled with the gas; carbonate of barium is then added in excess; and the whole is left to stand for twelve or eighteen hours, and shaken up from time to time. The precipitate, consisting of sesquioxide of cobalt and carbonate of barium, is then collected on a filter, and washed with cold water. The filtered liquid, which has a pure green colour, contains all the nickel without a trace of cobalt. The precipitate is boiled with hydrochloric acid to convert the sesquioxide of cobalt into protoxide, and dissolve it together with the baryta; the latter is then precipitated by sulphuric acid, and the cobalt from the filtrate by potash. The nickel is also precipitated by potash, after the removal of any baryta that the solution may contain by sulphuric acid. This method, if properly executed, gives very exact results. The chief precautions to be attended to, are to add a large excess of chlorine, and not to filter too soon, because the precipitation of sesquioxide of cobalt by carbonate of barium takes a long time.

According to Henry, *bromine* may be used in the preceding process instead of chlorine as the oxidising agent.

Liebig has given several methods of separating these two metals, founded on the difference of their reactions with *cyanide of potassium*. 1. The oxides of the two metals are treated with hydrocyanic acid and then with potash, and the liquid warmed till the whole is dissolved (pure cyanide of potassium, free from cyanate, may also be used as the solvent). The reddish-yellow solution is boiled to expel free hydrocyanic acid, whereupon the cobaltocyanide of potassium ($KCoCy^2$), formed in the cold, is converted into cobalticyanide ($K^3Co^2Cy^6$), while the nickel remains in the form of cyanide of nickel and potassium ($KNiCy^2$). Pure and finely-divided red oxide of mercury is then added to the solution while yet warm, whereby the whole of the nickel is precipitated, partly as oxide, partly as cyanide, the mercury taking its place in the solution. The precipitate contains all the nickel, together with excess of mercuric oxide; after washing and ignition, it yields pure oxide of nickel. The filtered solution contains all the cobalt in the form of cobalticyanide of potassium. It is supersaturated with acetic acid, boiled with sulphate of copper, which precipitates the cobalt in the form of cobalticyanide of copper ($2Cu^3Co^2Cy^6.7H^2O$), and the precipitate retained in the liquid at a boiling-heat till it has lost its glutinous character. It is then washed, dried, ignited, and dissolved in hydrochloric acid mixed with a little nitric acid; the copper is precipitated by sulphydric acid; and the filtrate, after boiling for a minute to expel the excess of that gas, is mixed with boiling caustic potash to precipitate the cobalt (Ann. Ch. Pharm. lxv. 244).—2. Instead of adding the oxide of mercury, the solution containing the mixed cyanides may, after cooling, be supersaturated with chlorine, the precipitate of cyanide of nickel thereby produced being continually redissolved by caustic potash or soda. The chlorine produces no change in the cobalticyanide of potassium, but decomposes the nickel-compound, the whole of the nickel being ultimately precipitated in the form of black sesquioxide. (Ann. Ch. Pharm. lxxxvii. 128.)

Liebig's first method (*ibid.* xli. 291), which consisted in treating the solution of the mixed cyanides with excess of hydrochloric or sulphuric acid, whereby the nickel was precipitated as cobalticyanide of nickel, leaving a solution of cobalticyanide of potassium, has been found, both by himself and others, not to give perfectly satisfactory results. The method by oxalic acid (p. 1040), and the precipitation of nickel from an ammoniacal solution of the two metals by potash (see NICKEL) are not sufficiently accurate for quantitative analysis.

F. Claudet separates cobalt from nickel and other metals in the form of the ammonio-compound described on page 1052, that compound being very insoluble, while corresponding compounds of the other metals do not appear to be formed under the same circumstances.

From **uranium**, in the state of sesquioxide, cobalt, as protoxide, may be separated by means of carbonate of barium, which throws down the uranic oxide and leaves the cobalt in solution. (For other modes of separation, see URANIUM.)

From **zinc**, cobalt may also be easily separated by precipitation with *nitrite of potassium*. Another mode of separation is: Convert the two metals into chlorides, and reduce the chloride of cobalt with hydrogen, as described for the separation of cobalt from manganese; the chloride of zinc then remains unaltered, and may be dissolved out. Thirdly, the metals may be precipitated by carbonate of sodium, the carbonates dissolved in a large excess of acetic acid, and sulphydric acid gas passed through the solution. The zinc is thereby precipitated as sulphide, while the cobalt remains dissolved. To ensure complete separation, it is necessary to add a large excess of acetic acid. Fourthly, the separation may be effected by precipitating the cobalt as sesquioxide, by means of peroxide of lead (p. 1044).

5. *Valuation of Cobalt-ores.*—The value of a cobalt-ore is estimated either by the amount of protoxide that it will yield, or by its power of imparting a blue colour to glass and enamel. (For the latter mode of valuation we refer to the article SMALT.)

To estimate the quantity of protoxide contained in a cobalt ore, the ore may be treated by either of the methods already given (pp. 1039, 1040), to separate the arsenic, copper, iron, &c., the cobalt being afterwards separated from the nickel, and estimated by either of the processes described on pp. 1044, 1045.

(For Plattner's method of estimation in the dry way, see his *Treatise on the Blowpipe*, translated by Muspratt, also *Kerl's Hüttenkünde*, iii. [1] 340, 342).

6. *Atomic Weight of Cobalt.*—Dumas has determined the atomic weight of cobalt by the quantity of silver required to decompose a known weight of the chloride. Pure metallic cobalt was dissolved in nitro-muriatic acid, the solution evaporated to dryness, keeping the hydrochloric acid continually in excess; the residue ignited in a stream of hydrochloric acid gas, or else heated in vacuo; and the chloride of cobalt thus obtained was decomposed by nitrate of silver. Five experiments thus made gave for the atomic weight of cobalt numbers varying from 29·50 to 29·59. Dumas regards 29·5 as the correct number (Ann. Ch. Pharm. cxiii. 24). This agrees with the original determination of Rothof (Pogg. Ann. viii. 185), which was made by converting a known weight of the protoxide into chloride, and then precipitating by nitrate of silver. Schneider (Pogg. Ann. ci. 317), from the analysis of the oxalate, estimated the atomic weight of cobalt at 30; but the number 29·5 is generally regarded as correct.

COBALT, EARTHY, or *Asbolan.*—A variety of wad or earthy manganese, containing oxide of cobalt. (See MANGANESE, OXIDES OF, and WAD.)

COBALT, FLUORIDE OF, CoF, may be obtained by dissolving cobaltous oxide or carbonate in aqueous hydrofluoric acid. The solution yields by evaporation small irregular rose-coloured crystals containing $CoF.H^2O$. The compound dissolves without decomposition in water containing free hydrofluoric acid, or in a small quantity of pure water; but with a larger quantity of water, it is resolved into an acid liquid containing cobalt, and an insoluble pale red basic salt consisting of $2Co^4F^2O.H^2O$. or $2\,(CoO.CoF) + HO$.

Fluoride of cobalt unites with the fluorides of ammonium and potassium, forming sparingly soluble double salts which crystallise in pale red granular crystals. (Berzelius.)

COBALT, IODIDE OF, CoI, is produced by digesting finely divided metallic cobalt with iodine and water, the mixture becoming heated to the boiling point. With a small quantity of water, it forms a green, and with a larger quantity, a red solution, and remains, on evaporation, as a dark green deliquescent mass soluble in alcohol. (Erdmann, J. pr. Chem. vii. 354.)

Ammonio-iodides of Cobalt.—Iodide of cobalt absorbs 3 at. ammonia-gas, forming the compound, $CoI.2NH^3$, which is a reddish-yellow powder. A concentrated solution of iodide of cobalt forms with ammonia a reddish-white precipitate which dissolves on heating, leaving only a few green flocks. The solution deposits small rose-coloured crystals, which, as well as the reddish-white precipitate, consist of $CoI.2NH^3$, but appear also to contain water. When dried, they give off ammonia, turn brown and afterwards green. Water decomposes them, liberating ammonia and depositing a green powder. A dilute solution of iodide of cobalt forms with ammonia a blue precipitate which turns green when exposed to the air, and a brown solution. (Rammelsberg, Pogg. Ann. xlviii. 155.)

COBALT, OXIDES OF. The following oxides of cobalt are known:

Protoxide or cobaltous oxide	Co^2O or CoO
Sesquioxide or cobaltic oxide	Co^4O^3 or Co^2O^3
Intermediate oxides	Co^6O^4 or Co^3O^4 $Co^{12}O^7$ or Co^6O^7 $Co^{16}O^9$ or Co^8O^9

The protoxide is a strong, the sesquioxide a weak base. According to Frémy, the oxide Co^6O^4 is also a salifiable base, which unites directly with acetic acid and exists in some of the ammoniacal salts of cobalt. Frémy has also obtained salts of this nature containing a dioxide of cobalt, Co^2O^2.

Protoxide of Cobalt or *Cobaltous Oxide*, Co^2O.—This oxide is obtained by igniting cobaltous hydrate or carbonate in close vessels; by igniting the protochloride in a stream of aqueous vapour (Schwarzenberg); also, mixed in various proportions with sesquioxide, when finely divided cobalt burns in the air, or when the compact metal is heated to redness in the air. The pure protoxide is a light greenish-grey or olive-green non-magnetic powder. It is reduced to the metallic state at a red heat by hydrogen, charcoal, carbonic oxide, potassium, and sodium. When heated with sulphur, it is converted into sulphide of cobalt and sulphurous anhydride; and with sulphydric acid, it yields water and sulphide of cobalt.

Hydrated cobaltous oxide, or Cobaltous hydrate, CoHO, or *CoO.HO*, is produced when a cobaltous salt is decomposed by potash out of contact of air. A blue basic salt is first produced which changes gradually at ordinary temperatures, quickly, on boiling, into the rose-coloured hydrate. If the cobalt-solution be dropped into strong boiling potash-ley, the change from blue to red is almost too rapid to be traced. Cobaltous hydrate is a powder of a dingy rose-red colour, which gives off water at 100° C., and is converted into the protoxide if the air be excluded, into a higher oxide if exposed to the air. It dissolves readily in acids, forming the cobaltous salts.

Sesquioxide of Cobalt, Cobaltic Oxide, Co^4O^3, is formed when chlorine is transmitted through water in which the hydrated protoxide is suspended, or when a salt of the protoxide is precipitated by a solution of chloride of lime. In the former case, water is decomposed by the chlorine, and hydrochloric acid produced, while the oxygen of the water peroxidises the cobalt:

$$2Co^2O + H^2O + Cl^2 = Co^4O^3 + 2HCl.$$

The sesquioxide of cobalt is precipitated as a black hydrate, which, when cautiously heated to 600° or 700° C., yields the black anhydrous oxide. When sesquioxide of cobalt is digested in hydrochloric acid, chlorine is evolved, and the protochloride formed. Exposed to a low red heat, the sesquioxide loses oxygen, and the compound oxide, $Co^2O.Co^4O^3$, is produced (Hess). When protoxide of cobalt is calcined with a borax glass, at a moderate heat, it absorbs oxygen, and a black mass is obtained, which, mixed with manganic oxide, serves as a black colour in enamel painting.

Sesquioxide of cobalt acts as a weak base. Phosphoric, sulphuric, nitric, and hydrochloric acids dissolve its hydrate in the cold, without decomposition at first, but the resulting salts are afterwards reduced to salts of the protoxide. A protosalt of cobalt containing a small quantity of a sesquisalt is somewhat deepened in colour. The most permanent of the sesquisalts is the acetate; the hydrated sesquioxide while yet moist dissolves in acetic acid, slowly but completely. The solution, which has an intense brown colour, forms a brown precipitate with *alkalis* and *alkaline carbonates*. With *ferrocyanide of potassium*, it forms a dark precipitate, which, if the precipitant is in excess, gives up cyanogen to it, converting it into ferricyanide of potassium and being itself converted into green ferrocyanide of cobalt. Alkaline *oxalates* colour the solution yellow, forming an oxalate of the oxide Co^3O^2, or Co^6O^4.

Cobaltoso-cobaltic oxides.—*a.* The oxide, Co^3O^2 or $Co^6O^4 = Co^2O.Co^4O^3$, is obtained in the free state by heating the nitrate or oxalate of cobalt, or the hydrated sesquioxide, to redness in contact with the air (Hess, Rammelsberg); but according to Beetz and Winkelblech, the oxide thus obtained is $Co^{12}O^7$. When the residue obtained by gently igniting the oxalate in contact with the air is digested in strong boiling hydrochloric acid, the oxide Co^3O^2 remains in hard, brittle, greyish-black microscopic octahedrons having a metallic lustre. The same crystalline compound is obtained by strongly igniting dry protochloride of cobalt, alone or mixed with sal-ammoniac, in dry air or oxygen gas. (Schwarzenberg.)

This oxide, according to Frémy, is also a salifiable base. The corresponding oxalate has already been mentioned. The acetate is obtained by digesting in dilute acetic acid the hydrated oxide obtained by continued action of oxygen on the blue precipitate thrown down from ordinary cobalt-salts by potash not in excess. Frémy also states that when chlorine is passed into the solution of ordinary acetate of cobalt, a brownish-yellow salt is formed containing the base $Co^6Cl^2O^3$, or Co^6O^4 in which 1 at. O is replaced by Cl^2. This chlorine-base exists also in some of the ammonio-compounds of cobalt (p. 45).

b. The oxide, $Co^{12}O^7 = 3Co^2O.Co^4O^3$, is said by Winkelblech to be formed by keeping the hydrated protoxide at a red heat in the air for a considerable time, or by first reducing it to the metallic state by heating it very gently in a stream of hydrogen, and then burning it again by passing air through the tube. According to Rammelsberg, however (Pogg. Ann. lxxiii. 93), the oxide obtained by either of these processes is Co^3O^4.

c. Another oxide, $Co^{16}O^9 = 6Co^2O.Co^4O^3$, is said to be obtained by precipitating cobaltic nitrate with ammonia, exposing the liquid to the air till the blue precipitate turns green, then suspending the precipitate in water, and exposing it to the air for a month till it turns quite yellow. But the yellow hydrate thus formed always retains a trace of nitric acid, which cannot be removed even by long contact with water.

A *cobaltic acid* (or anhydride), Co^6O^5, is obtained in combination with potash, by strongly igniting the oxide, Co^3O^2, or the protoxide or carbonate, with pure hydrate of potassium. A crystalline salt is then formed which, when dried at 100° C., contains $K^2O.3Co^6O^5 + 3aq.$, and gives off 1 at. water at 130°. (Schwarzenberg.)

Dioxide of Cobalt, CoO, or Co^2O^2, has not been obtained in the free state, but may be supposed to exist in the oxycobaltic-salts (p. 1056).

COBALT, OXYSULPHIDE OF, Co^4SO, or *CoS.CoO.*—Produced by igniting the sulphate in hydrogen gas. Water and sulphurous acid escape, and there remains a dark grey sintered mass which is not altered by the further action of the hydrogen. Cold hydrochloric acid decomposes it, dissolving oxide of cobalt and leaving sulphide; but if heat be applied, the sulphide likewise dissolves. (Arfvedson.)

COBALT, OXYGEN-SALTS OF.—The cobaltous salts are produced by dissolving metallic cobalt in the stronger acids; by the action of acids on the protoxide, hydrate, or carbonate; by boiling the hydrate or carbonate in solutions of ammonia-salts, ammonia being then evolved and a cobaltous solution formed; and by precipitation. The carbonate, phosphate, borate, silicate, and those which contain metallic acids, are insoluble in water; most of the others are soluble. The insoluble salts have a violet or peach-blossom colour; the dissolved salts a rose colour. The neutral solutions redden litmus slightly. For their reactions and those of the cobaltic salts, see pp. 1043, 1044.

COBALT, PHOSPHIDES OF.—The *tricobaltic phosphide*, or *tricobalt-phosphine*, Co^6P, was obtained by H. Rose as a grey powder, on passing hydrogen gas over basic phosphate of cobalt ignited in a porcelain tube. It is also produced by the action of phosphoretted hydrogen on chloride of cobalt.

Another phosphide containing a very large excess of cobalt is produced when pieces of phosphorus are thrown on red-hot cobalt; when 1 pt. of the metal is ignited with 7 pts. glacial phosphoric acid and $\frac{1}{16}$ charcoal powder; and when a mixture of 70 pts. metallic cobalt or oxide of cobalt, 100 bone-ash, 50 pounded quartz, and 10 charcoal is exposed for an hour to the heat of a blast-furnace. The compound prepared by the first or second method is bluish-white, with metallic lustre, brittle, of acicular structure, more fusible than cobalt, contains 6 per cent. phosphorus, and burns to a dark blue glass when heated (Pelletier). The product obtained by the third process is of a shining white colour, very fusible, non-magnetic, and often has needle-shaped crystals in its cavities.

COBALT, RED. Syn. with COBALT-BLOOM (p. 1057).

COBALT, SELENIDE OF. Heated cobalt unites with selenium, forming a grey mass, which exhibits metallic lustre and crystalline structure, and melts at a red heat; the combination is attended with ignition. (Berzelius.)

COBALT, SULPHIDES OF. The *protosulphide*, Co^2S, or *CoS*, occurs native as Syepoorite, a massive mineral of steel-grey colour inclining to yellow, found disseminated in grains or veins in ancient schists, associated with magnetic pyrites, at Syepoor, near Rajpootanah, in North-west India. It is employed by the Indian jewellers to give a rose-colour to gold. According to Middleton's analysis Phil. Mag. [3] xxxviii. 352), it contains 35·36 S, and 64·64 Co, agreeing closely with the formula Co^2S.

The protosulphide may be prepared by throwing sulphur on red-hot cobalt contained in a retort, also by heating the protoxide with sulphur, and by igniting cobaltous sulphate to whiteness in a crucible lined with charcoal. As thus obtained, it is a grey laminar mass having the metallic lustre; according to Berthier, it is magnetic. In the wet way, it is produced by precipitating cobaltous acetate with sulphydric acid or any neutral cobaltous solution with an alkaline sulphide. The precipitate is a black powder which gives off water when heated, and in the moist state slowly oxidises in the air, being converted into sulphate. It is insoluble in alkalis and alkaline sulphides, soluble in concentrated mineral acids, insoluble or nearly so in dilute acids. It unites with acid sulphides, forming sulphur-salts, which are all insoluble in water. According to Anthon, it decomposes the solutions of other metals, *e. g.* iron, nickel, copper, and silver, a sulphide of the other metal being precipitated and the cobalt taking its place in the solution. This appears somewhat inconsistent with the action of dilute hydrochloric acid on a mixture of the sulphides of iron and cobalt, which, according to H. Rose (p. 1044), affords a method of completely separating cobalt from iron. It unites with peroxide of cobalt, forming an oxysulphide (*vid. sup.*).

Sesquisulphide of Cobalt, or *Cobaltous Sulphide*, is obtained by precipitating cobaltic acetate with sulphydric acid, or by heating cobaltic hydrate, but not to redness, in an atmosphere of the same gas. It has a dark grey colour. According to Fellenberg (Pogg. Ann. l. 73), it is obtained in graphitic laminæ by igniting the protoxide with sulphur and an alkali. *Linnæite* or *cobalt-pyrites* is commonly stated to be a sesquisulphide, but its composition approaches more nearly to that of the following compound:

Cobaltoso-cobaltic Sulphide, Co^3S^2, or $Co^2S.Co^4S^3$, or $Co^3S^4 = CoS.Co^2S^3$.—*Linnæite* from Müsen, near Siegren, in Prussia, has nearly this composition, yielding, according to Wernekink's analysis, 43·25 S, 53·35 Co, 0·97 Cu, and 2·30 Fe = 98·87, the formula requiring 42 S and 58 Co (Dana, ii. 66). In most varieties of this mineral, however, the cobalt is replaced to a greater extent by copper or nickel. (See LINNÆITE.)

Oxysulphide of cobalt heated in sulphydric acid gas yields a product which appears to be a sulphide intermediate in composition between the proto- and sesqui-sulphides. (Anthon.)

Disulphide of Cobalt, CoS, or CoS^2, may be supposed to exist in combination with arsenide of cobalt in cobaltine (*q. v.*)

COBALT-BASES, AMMONIACAL. (F. Claudet [1857], Phil. Mag. [4] ii. 253.—Genth, Ann. Ch. Pharm. lxxx. 275.—Frémy, Ann. Ch. Phys. [3] xxxv. 257.—Rogojski, *ibid.* xli. 445.—Gregory, Ann. Ch. Pharm. lxxxvii. 125.—Gibbs and Genth, Smithsonian Contributions, 1856; Sill. Am. J. [2] xxxiii. 234, 319; xxxiv. 96; Ann. Ch. Pharm. civ. 150, 295; Jahresber, f. Chem. 1857, 227.—Künzel, J. pr. Chem. lxxii. 209).—Cobaltous salts treated with ammonia in a vessel protected from the air unite with the ammonia, forming compounds which may be called ammonio-cobaltous salts. Most of them contain 3 at. ammonia to 1 at. of the cobalt-salt; thus the chloride contains $CoCl.3NH^3 + \frac{1}{2}aq.$; the nitrate $CoNO^3.3NH^3 + aq.$ They are generally crystallisable and of a rose-colour, soluble without decomposition in ammonia, but decomposed by water, with formation of a basic salt (Frémy). H. Rose, by treating dry chloride of cobalt with ammonia-gas, obtained the compound $CoCl.2NH^3$, and in like manner an ammonio-sulphate has been formed containing $Co^2SO^4.6NH^3$.

When an ammoniacal solution of cobalt is exposed to the air, oxygen is absorbed, the liquid turns brown (p. 37), and new salts are formed containing a higher oxide of cobalt (either Co^4O^5 or Co^2O^3), and therefore designated generally as peroxidised ammonio-cobalt salts. Several of them containing different bases are often formed at the same time.

Most of the peroxidised ammonio-cobalt salts are composed of sesquisalts of cobalt (cobaltic salts), united with 2 or more molecules of ammonia. The composition of the neutral salts may be illustrated by the chlorides, as in the following table:

Diammonio-cobaltic chloride	$Co^2Cl^3.\ 2NH^3$
Triammonio-cobaltic chloride	$Co^2Cl^3.\ 3NH^3$
Tetrammonio-cobaltic chloride	$Co^2Cl^3.\ 4NH^3$
Pentammonio-cobaltic chloride	$Co^2Cl^3.\ 5NH^3$
Hexammonio-cobaltic chloride	$Co^2Cl^3.\ 6NH^3$

The formulæ of the corresponding neutral nitrates are deduced from the preceding by substituting NO^3 for Cl; for the sulphates, oxalates, and other dibasic salts, the number of atoms of cobalt and ammonia must of course be doubled. Thus, *pentammonio-cobaltic sulphate* = $Co^4(SO^4)^3.10NH^3$. There are also several acid and basic salts of the same ammonio-molecules, the formulæ of which will be given further on. Further, there is a class of salts containing the elements of nitric oxide in addition to ammonia, *e. g. pentammonio-nitroso-cobaltic oxychloride* = $Co^4Cl^4O.10NH^3.2NO$. Lastly, Frémy has obtained ammoniacal compounds (oxycobaltic salts) containing salts of cobalt corresponding to the dioxide Co^2O^2.

DIAMMONIO-COBALTIC SALTS.—The sulphite of this group is obtained by adding acid sulphite of ammonium to an aqueous solution of pentammonio-cobaltic chloride containing a very small quantity of ammonia, till the odour of sulphurous acid becomes distinctly perceptible; on leaving the solution to stand for some time, the sulphite separates in brown, nearly insoluble octahedrons, containing $Co^4(SO^3)^3.4NH^3 + 5aq.$ (Künzel.)

TRIAMMONIO-COBALTIC SALTS.—When a solution of pentammonio-cobaltic chloride containing a little ammonia, is mixed with so much acid sulphite of ammonium that the liquid does not smell either of ammonia or of sulphurous acid, it changes colour from red to deep yellow, and deposits *triammonio-cobaltic sulphite*, $Co^4(SO^3)^3.6NH^3 + aq.$, as a yellow powder or in crystalline needles, according to the temperature and concentration of the liquid. It is insoluble in cold water, and is slowly decomposed by boiling with water. Its formation is expressed by the equation:

$$2(Co^2Cl^3.5NH^3) + 2NH^3 + H^2O + 6(NH^4.H.SO^3) =$$
$$[Co^4(SO^3)^3.6NH^3 + H^2O] + 6NH^4Cl + 3[(NH^4)^2.SO^3]. \quad \text{(Künzel.)}$$

TETRAMMONIO-COBALTIC SALTS. Frémy's *Fusco-cobaltic salts.*—These salts are formed when an ammoniacal solution of a cobaltous salt is exposed to the air, and by the action of water on oxy-cobaltic salts. They are brown, and mostly uncrystallisable, but may be obtained in the solid state by precipitation with alcohol or excess of ammonia. They are slowly decomposed by boiling with water, but quickly on addition of an alkali, with evolution of ammonia and precipitation of cobaltic hydrate. They are basic salts, the *nitrate* containing $Co^4O^3.2N^2O^5.8NH^3 + H^2O$, or $\left.\begin{matrix}(NO^2)^2\\(Co^2)'''.H\end{matrix}\right\}O^3.4NH^3$, and the *hyposulphate* $Co^4O^3.2S^2O^5.8NH^3$.

Pentammonio-cobaltic Salts. (Frémy, *loc. cit.*; Gibbs and Genth, *loc. cit.*)—These salts may be divided into two groups, the *Roseo-cobaltic salts*, which have a red colour, varying from brick to rose-red, and the *Purpureo-cobaltic salts*, which are purple, or violet-red. The salts of both groups contain 5 at. NH^3 to 2 at. cobalt, but the roseo-cobaltic salts are, for the most part, neutral, while the purpureo-cobaltic salts are either basic or acid; in some cases, however, as with the chlorides, the difference consists merely in the presence or absence of water, the purple salts being anhydrous, and the red hydrated.

The pentammonio-cobaltic salts are produced by the direct oxidation of ammoniacal solutions of cobaltous salts, as when these solutions are exposed to the air, the red and purple salts being often produced together, the latter especially when the temperature is rather high, and the solution contains a free ammoniacal salt. The purpureo-cobaltic salts are likewise formed by the action of acids on xantho-cobaltic salts (p. 1054).

Pentammonio-cobaltic salts are nearly insoluble in cold water, but soluble in warm water slightly acidulated; the purple salts are in general less soluble than the red. Their taste is purely saline, not metallic. When heated in the dry state, they decompose, giving off ammonia, and yielding an ammonium-salt and a cobaltous salt. Their aqueous solutions, when not acidulated, are decomposed by boiling, giving off ammonia and depositing a hydrated cobaltoso-cobaltic oxide. The solutions of roseo-cobaltic salts boiled with strong acids, are converted into purpureo-cobaltic salts.

Chlorides. 1. *Hydrated Pentammonio-cobaltic chloride*, or *Roseo-cobaltic chloride*, $Co^2Cl^3.5NH^3 + aq.$—This salt was discovered by Claudet and by Genth, in 1851, being the first ammonio-cobaltic salt obtained; the formulæ originally assigned to it, however, gave a somewhat different view of its constitution. It is the most frequent product of the oxidation of an ammoniacal solution of protochloride of cobalt by exposure to the air, the liquid assuming first a brown, and then a red colour, and often, especially if the ammonia and the chloride of cobalt are impure, depositing a small quantity of cobaltic hydrate. The presence of sal-ammoniac in the solution does not facilitate its formation. The reddened solution mixed with strong hydrochloric acid, and carefully guarded against rise of temperature, deposits roseo-cobaltic chloride as a brick-red precipitate, which, after washing with strong hydrochloric acid, then with ice-cold water, and drying at the lowest possible temperature, contains $Co^2Cl^3.5NH^3 + H^2O$. It dissolves in water either cold or warm, with dark-red colour, which, however, changes after a while, especially if the solution be acidulated with hydrochloric acid and heated, to violet-red. The pure aqueous solution when boiled gives off ammonia and deposits hydrated cobaltoso-cobaltic oxide, $Co^3O^4 + xH^2O$.

Roseo-cobaltic chloride forms double salts with the chlorides of the more electronegative metals.

Purpureo-cobaltic chloride, $Co^2Cl^3.5NH^3$.—It has already been mentioned, that the red solution of roseo-cobaltic chloride changes to violet when heated with hydrochloric acid. The same change takes place slowly in the dry salt. This purple modification is often formed, together with the red one and sometimes alone, during the oxidation of ammonio-cobaltous chloride, especially if the temperature is rather high, and the solution contains sal-ammoniac. By boiling the oxidised liquid with excess of hydrochloric acid, and crystallising the precipitated carmine-coloured powder from water acidulated with the same acid, the purpureo-cobaltic chloride is obtained pure. It may also be prepared by boiling a xantho-cobaltic salt (p. 1054),—the nitrate being best adapted for the purpose—with hydrochloric acid; lastly, by boiling any other purpureo-cobaltic salt with hydrochloric acid. It forms small violet-red or purple crystals, which, according to Dana, are dimetric combinations, $P \,.\, \infty P\infty \,.\, P\infty$. Length of principal axis = 1·9016. $P : P$ in the lateral edges = 114° 8′; in the terminal edges, 107° 12′. Specific gravity 1·802. The crystals are anhydrous, nearly insoluble in cold water, soluble without decomposition in boiling water slightly acidulated with hydrochloric acid. A larger addition of hydrochloric acid, or a solution of an alkaline chloride, precipitates it slowly in the cold, quickly on boiling. The solution yields with *dichloride of platinum* a brown-red precipitate, composed of flat microscopic needles, containing $Co^2Cl^3.5NH^3.2PtCl^2$.

Cyanides.—*Roseo-cobaltic cobalticyanide*, $(Co^2Cy^3.5NH^3).Co^2Cy^3 + \frac{3}{2}H^2O$, is precipitated by cobalticyanide of potassium from roseo-cobaltic solutions, in cherry-coloured crystals apparently having the form of rhombic prisms, insoluble in cold water, decomposed by hot water. The *ferricyanide*, $(Co^2Cy^3.5NH^3).Fe^2Cy^3 + \frac{3}{2}H^2O$, is an orange-coloured crystalline precipitate, possessing similar properties.

Oxides.—*Roseo-cobaltic oxide* is obtained in solution by decomposing the solution of the chloride with oxide of silver, or better—since chloride of silver is somewhat soluble in roseo-cobaltic chloride—by decomposing the sulphate with baryta-water.

The solution has an alkaline taste and reaction, absorbs carbonic acid from the air, and decomposes with facility.—*Purpureo-cobaltic oxide*, obtained in like manner, forms a violet-red alkaline solution, which absorbs carbonic acid from the air, and suffers decomposition when concentrated.

Nitrates.—The *neutral* or *roseo-cobaltic nitrate*, is obtained, as a shining yellow precipitate, when an ammoniacal solution of cobaltous nitrate is left to oxidise in the air, (crystals of Frémy's oxycobaltic nitrate are frequently also formed at first, but subsequently disappear). The deep wine-red liquid yields, by spontaneous evaporation, red crystals, containing $Co^2(NO^3)^3.5NH^3. + H^2O$, easily soluble even in cold water. According to Dana, they are monoclinic combinations $\infty P\infty . [\infty P\infty] . + P\infty . - P\infty . \infty P$. Inclination of faces, $\infty P : \infty P$ in the clinodiagonal principal section = 103°; $\infty P\infty : P\infty = 140° 30'$; $\infty P\infty : -P\infty = 136°$. From the solution of these crystals, or from the original oxidised ammoniacal solution, nitric acid added in the cold throws down a brick-red precipitate of the hydrated salt; but on boiling the liquid with nitric acid, the *anhydrous nitrate*, $Co^2(NO^3)^3.5NH^3$, is thrown down as a violet-red crystalline precipitate. It dissolves in dilute ammonia and separates from the solution by spontaneous evaporation in dimetric crystals $P . P\infty . \infty P . \infty P\infty . 3P3$. Inclination of $P : P$ in the lateral edges, = 82° 40′. This anhydrous salt is nearly insoluble in cold water, more soluble in hot water, but the solution is easily decomposed by heat; addition of nitric acid prevents the decomposition. The anhydrous salt explodes when heated, giving off nitrous vapours, and leaving black sesquioxide of cobalt.—A *basic nitrate*, probably $Co^4O^3.2N^2O^5.10NH^3 + 7H^2O$ or $\left.\begin{matrix}(NO^2)^2 \\ (Co^2)'''.H\end{matrix}\right\}O^3.5NH^3 + 3H^2O$, is obtained in purple scaly crystals, when a solution of the hydrated neutral nitrate, mixed with a large quantity of nitrate of ammonium and a little free ammonia is left to evaporate. These crystals are decomposed by solution in water, and when boiled with hydrochloric acid, yield with brisk effervescence, a purple-red solution and a deposit of purpureo-cobaltic chloride (Gibbs and Genth). Both this basic nitrate and the anhydrous neutral nitrate appear to belong to the so-called purpureo-cobaltic group. Künzel, by exposing an ammoniacal solution of cobaltous nitrate to the air till it had acquired a dark olive-brown colour, and then adding nitrate of ammonium, obtained a yellow crystalline precipitate, to which he assigns the formula $2(Co^4O^3.10NH^3).5N^2O^5$.

Oxalates.—*Roseo-cobaltic oxalate* is precipitated by oxalate of ammonium from a solution of the chloride immediately, from the nitrate very slowly; it may be purified by recrystallisation from water containing ammonia. The cherry-coloured crystals, which are rhombic prisms of 101° 48′, with a brachydome of 108° 54′, contain $\left.\begin{matrix}(C^2O^2)''^3 \\ (Co^4)^{vi}\end{matrix}\right\}O^6.10NH^3 + 6aq.$; they are nearly insoluble in pure water. The *basic*, or *purpureo-cobaltic oxalate*, $\left.\begin{matrix}(C''O^2)^2 \\ (Co^4)^{vi}\end{matrix}\right\}O^5.5NH^3 + 3aq.$, separates in violet-red needles on adding oxalate of ammonium to a solution of purpureo-cobaltic chloride.

Oxalo-sulphates.—An *acid oxalo-sulphate*, $Co^4O^3.2C^2O^3.2SO^3.10NH^3 + 3H^2O$ or $\left.\begin{matrix}(C^2O^2)'' \\ (SO^2)'' \\ (Co^2)'''H\end{matrix}\right\}O^4.5NH^3 + H^2O$, is obtained in brick-red, ill-defined needles by boiling roseo-cobaltic sulphate for several hours with excess of oxalic acid. The solution of this salt assumes a violet-red colour on addition of ammonia, and, if exactly neutralised, yields by evaporation prismatic crystals of a *basic oxalo-sulphate*, $\left.\begin{matrix}(C^2O^2)'' \\ (SO^2)'' \\ (Co^4)^{vi}\end{matrix}\right\}O^5.10NH^3 + 7H^2O$, which is more soluble than the acid salt, and is easily decomposed by boiling.

Sulphates.—*Roseo-cobaltic sulphate* is generally (but not always) produced in an ammoniacal solution of cobaltous sulphate by atmospheric oxidation, the liquid becoming first brown and then dark red. On carefully adding sulphuric acid to this red solution, the sulphate is deposited as a brick-red crystalline powder, which may be purified by washing with cold water and recrystallisation from a slightly acidulated solution. The cherry-coloured crystals, containing $\left.\begin{matrix}(\overset{''}{SO^2})^3 \\ (Co^4)^{vi}\end{matrix}\right\}O^6.10NH^3 + 5H^2O$, are, according to Dana, dimetric combinations, $P . 2P . P\infty . 0P . \infty P . \infty P\infty$. Inclination of $P : P$ in the terminal edges = 107° 20′. Length of principal axis = 1·0866. The salt is nearly insoluble in cold water, sparingly soluble in boiling water, and crystallises from the solution on cooling. It dissolves in dilute ammonia, and crystallises unaltered from the purple-red solution. On boiling the neutral salt, a dark brown powder separates, which, after drying in the air, contains $Co^2O^3 + 3H^2O$, while luteo-cobaltic sulphate remains in solution, being, however, partially decomposed.

An *acid (purpureo-cobaltic) sulphate*, $Co^4O^3.4SO^3.10NH^3 + 5H^2O$, or $\left.\begin{matrix}(S''O^2)^2\\(Co^2)'''H\end{matrix}\right\}O^4.5NH^3 + 2H^2O$, is obtained by mixing the anhydrous chloride (p. 46) with oil of vitriol to a thick pulp, diluting the solution with twice its bulk of water, as soon as the evolution of hydrochloric acid has ceased, then washing the violet-red needles which separate with a little cold water, and pressing them; also by adding oil of vitriol to roseo-cobaltic sulphate till an oily liquid is produced; digesting this for an hour or two, taking care to avoid escape of oxygen, diluting the evolved purple solution with an equal bulk of water, and recrystallising. The crystals are red prisms; according to Dana, rhombic hemihedral combinations, $\infty P . \infty\breve{P}\infty . \frac{1}{2}\breve{P}\infty . \frac{\breve{P}2}{2} . \infty\breve{P}2$. Inclination of $\infty P : \infty P = 106°$; $\frac{1}{2}\breve{P}\infty : \frac{1}{2}\breve{P}\infty$, on the principal axis $= 122° 42'$. The salt has an acid taste and reaction, dissolves easily in water, but is quickly converted into the neutral (roseo-cobaltic) sulphate; especially by slow evaporation of a solution prepared with the aid of heat. (Gibbs and Genth.)

Sulphite. $\left.\begin{matrix}(\overset{\prime\prime}{SO})^2\\(Co^4)^{vi}\end{matrix}\right\}O^6.5NH^3 + \frac{2}{3}H^2O$.—Black-brown, heavy, amorphous precipitate, formed when sulphurous acid gas is passed through a dilute ammoniacal solution of pentammonio-cobaltic chloride; also by passing the gas through water in which tri-ammonio-cobaltic sulphite (p. 1051) is suspended. It is insoluble in cold water, and is decomposed by boiling water. (Künzel.)

NITROSO-PENTAMMONIO-COBALTIC, or XANTHO-COBALTIC SALTS. (Gibbs and Genth, *loc. cit.*)—These salts are produced by passing the nitrous vapours evolved from a mixture of nitric acid and starch or sawdust, into ammoniacal solutions of cobaltous salts, or into neutral, acid, or ammoniacal solutions of roseo- or purpureo-cobaltic salts. The gas is absorbed; fumes of carbonate of ammonia make their appearance; the liquid gradually assumes a dark reddish-brown colour, and then, on cooling, generally deposits a xantho-cobaltic salt.

Xantho-cobaltic salts are brownish-yellow, more soluble in water than the roseo- or purpureo-cobaltic salts, the dilute solutions having a yellow, the more concentrated solutions a dark brown colour. They decompose, though not easily, when these solutions are boiled sometimes also below the boiling temperature—giving off ammonia and depositing a dark-coloured heavy powder. The addition of a few drops of acetic acid prevents this decomposition; but, on adding a small quantity of an inorganic acid, nitric oxide gas is evolved, and a purpureo-cobaltic salt is formed, which, however, is difficult to separate from the undecomposed xantho-cobaltic salt.

The xantho-cobaltic salts appear to have the composition of sesquisalts of cobalt, associated with 5 or 10 at. NH^3, 1 or 2 at. NO, and 1 or 2 at. water.

The *chloride*, or rather *oxychloride*, $Co^4OCl^4.10NH^3.2NO + H^2O$, or $\left.\begin{matrix}(Cl^2O)''\\(Co^2)'''H\end{matrix}\right\}5NH^3.NO$, is not produced by either of the reactions just mentioned, but may be prepared by decomposing the sulphate with chloride of barium, and evaporating the filtrate at a gentle heat, after adding a few drops of acetic acid. It forms brownish-yellow, iridescent crystals. Its solution, mixed with *trichloride of gold*, yields a double salt, which, by recrystallisation from hot water, is obtained in brownish-yellow, iridescent prisms, containing $Co^4OCl^4.10NH^3.2NO.2AuCl^3 + 2H^2O$.—The *chloroplatinate*, $Co^4OCl^4.10NH^3.2NO.4PtCl^2 + 2H^2O$, is nearly insoluble in water, but may be crystallised from hot dilute hydrochloric acid. The *chloromercurate*, $Co^4OCl^4.10NH^3.2NO.8HgCl + 2H^2O$, is obtained by precipitation in pale brownish-yellow laminæ; by recrystallisation from hot slightly acidulated water, in brownish-yellow needles.

Xantho-cobaltic ferrocyanide, $Co^4OCy^4.10NH^3.2NO.2FeCy + 7H^2O$, is obtained by precipitating the nitrate with ferrocyanide of potassium (the solutions of the chloride and sulphate are merely clouded by that reagent) in orange-yellow prismatic crystals, which give up their water easily and without decomposition, are insoluble in cold water, and are decomposed by hot water.

The *nitrate*, which is a basic salt, containing $Co^4O^3.2N^2O^5.10NH^3.2NO + H^2O$, or $\left.\begin{matrix}(NO^2)^2\\(Co^2)'''H\end{matrix}\right\}O^3.5NH^3.NO$, forms light brownish-yellow quadratic prisms, having P : P in the lateral edges, between 100° 45′ and 101° 15′.

The *oxalate*, $Co^4O^3.2C^2O^3.10NH^3.2NO + 5H^2O = \left.\begin{matrix}(C^2O^2)''\\(Co^2)'''H\end{matrix}\right\}O^3.5NH^3.NO + 2H^2O$, is obtained by precipitation in yellow acuminated crystals, insoluble in cold, sparingly soluble in boiling water, decomposed by boiling.

The *sulphate*, $Co^4O^3.2SO^3.10NH^3.2NO + H^2O$ or, $\left.\begin{matrix}(SO^2)''\\(Co^2)'''H\end{matrix}\right\}O^3.5NH^3.NO$, crystallises in thin plates, apparently rhombic. It dissolves in strong sulphuric acid, giving off but little nitric oxide, and forming a red oily liquid, which gives off nitric oxide abundantly on addition of water, while the remaining liquid consists chiefly of ammonio-cobaltous sulphate, usually mixed with a small quantity of acid purpureo-cobaltic sulphate.

HEXAMMONIO-COBALTIC, or LUTEO-COBALTIC SALTS. (Frémy; Gibbs and Genth, *loc. cit.*)—These salts, discovered by Frémy, are often produced by the direct oxidation of ammonio-cobaltous solutions; frequently also by the decomposition of pentammonio-cobaltic salts, although their molecule contains an additional atom of ammonia. They are of yellow or brownish-yellow colour, more soluble in water than the roseo-cobaltic salts, and yield brownish-yellow solutions. They are very permanent in presence of acids, but are decomposed by continued heating with sulphuric acid; in neutral or alkaline solutions they are easily decomposed by boiling.

Luteo-cobaltic chloride, $Co^2Cl^3.6NH^3$, is often formed during the oxidation, by exposure to the air, of an ammoniacal solution of protochloride of cobalt mixed with a large quantity of coarsely-pounded sal-ammoniac (in other cases, the products are roseo and purpureo-cobaltic chloride); almost always, if the ammoniacal solution contains sulphate of cobalt as well as chloride: in the latter case, a salt is formed containing sulphuric and hydrochloric acids, and this, when boiled with hydrochloric acid and chloride of barium, yields a solution of luteo-cobaltic chloride. This salt, purified by repeated crystallisation, forms brownish orange-coloured crystals of specific gravity 1·7016. They belong to the trimetric system, and, according to Dana, exhibit the faces $\infty P \,.\, 0P \,.\, \bar{P}\infty \,.\, 3\breve{P}\infty$, two faces, $\infty\breve{P}3$, on one side only of the macrodiagonal, and four faces, $\frac{4}{3}P$, lying in one zone. Inclination of $\infty P : \infty P = 113° 16'$. It dissolves easily in boiling water, and separates for the most part as the solution cools. It is precipitated unaltered by hydrochloric acid and the chlorides of the alkali-metals. Boiling aqueous ammonia decomposes it slowly, with formation of chloride of ammonium and a dark brown oxide of cobalt.

Concentrated solutions of luteo-cobaltic chloride and dichloride of platinum, yield orange-coloured needles of a chloroplatinate containing $Co^2Cl^3.3PtCl^2.6NH^3 + 3$ aq.; dilute solutions deposit yellow needles of the same compound with $10\frac{1}{2}$ at. water; these, according to Dana, are monoclinic combinations $\infty P \,.\, \infty P\infty \,.\, 0P$. Inclination of $\infty P : \infty P$, in the clinodiagonal section, $= 107° 10'$; $0P : \infty P\infty = 114° 15'$. The crystals are often twins united by the face 0P.—*Trichloride of gold* forms with luteo-cobaltic chloride a yellow precipitate, consisting of small granular crystals, $Co^2Cl^3.AuCl^3.6NH^3$.

Luteo-cobaltic iodide, $Co^2I^3.6NH^3$, is thrown down by iodide of potassium from luteo-cobaltic solutions, as a yellow precipitate, nearly insoluble in cold water, moderately soluble in hot water, and separating in brownish-yellow crystals on evaporation. The bromide is obtained in like manner as a deep yellow precipitate, in other respects resembling the iodide.

Luteo-cobaltic cobalticyanide $(Co^2Cy^3)^2.6NH^3 + \frac{1}{3}H^2O$, is precipitated by cobalticyanide of potassium as a yellowish flesh-coloured precipitate composed of microscopic, oblique rhombic crystals. *Ferricyanide of potassium* forms an orange-yellow precipitate, exhibiting the same forms under the microscope.

Luteo-cobaltic oxide.—By decomposing the sulphate with baryta-water, a brownish-yellow alkaline solution is formed, which absorbs carbonic acid from the air, and is decomposed by evaporation, with evolution of ammonia and deposition of a black powder.

Luteo-cobaltic nitrate, $Co^2(NO^3)^3.6NH^3$, separates from an oxidised solution of ammonio-cobaltous nitrate in orange-coloured crystalline laminæ, the supernatant liquor being usually red and containing roseo-cobaltic nitrate. The salt, purified by recrystallisation, forms crystals belonging to the dimetric system, with the faces $P \,.\, 3P \,.\, 0P$. Angle of $P : P$ in the lateral edges $= 110° 20'$; of $3P : 3P$ in the same $= 153° 52'$. Length of principal axis for $P = 1·0161$.

Carbonates.—The *neutral carbonate*, probably $Co^4(CO^3)^3.12NH^3 + 7H^2O$, is obtained by decomposing a solution of the chloride with carbonate of silver, and leaving the liquid to evaporate, in rhombic crystals, $\infty P \,.\, \infty\breve{P}\infty \,.\, \breve{P}\infty$ Inclination of $\infty P : \infty P = 116° 50'$; $\breve{P}\infty : \breve{P}\infty$ on the principal axis $= 114° 16'$. If the air has had access to the solution, the crystals are generally mixed with those of the acid salt. The *acid carbonate*, $(Co^2)'''HC^2O^6.6NH^3 + \frac{5}{2}$aq., separates, on passing carbonic acid gas into the solution of the neutral salt, in large brown-red crystals, which, according to Dana, are monoclinic combinations, as $P \,.\, \infty P\infty \,.\, [\infty P\infty] \,.\, 0P \,.\, -P \,.\, +2P\infty$. Inclination of

$\infty P : \infty P$, in the clinodiagonal section, = 85° 54′; $0P : \infty P$ = 102° 20′; $0P : \infty P\infty$ = 71° 44′; $0P : -P$ = 139° 50′; $\infty P : +2P\infty$ = 111° 46′.

Oxalates.—The *neutral oxalate* is thrown down by oxalate of ammonia, as a reddish-yellow precipitate composed of slender needles, insoluble in water, easily soluble in oxalic acid, and separating therefrom in wine-yellow, efflorescent, prismatic crystals, containing $Co^4(C^2O^4)^3.12NH^3 + 4H^2O$. The *acid oxalate* was not obtained.

Luteo-cobaltic sulphate is obtained, mixed with the chloride, when an ammoniacal solution of cobaltous sulphate and chloride mixed with a large excess of coarsely pulverised sal-ammoniac, is left exposed to the air. The crystalline mass deposited at the bottom of the vessel is dissolved in hot water; the filtrate is acidulated with a few drops of sulphuric acid and treated with sulphate of silver; and the liquid, after filtration and concentration, is left to crystallise. The salt is also (though not constantly) produced by the action of strong ammonia on roseo-cobaltic sulphate, the change consisting simply in the assumption of 1 at. NH^3: also as a product of the decomposition of roseo-cobaltic sulphate (a salt of another base, not yet further examined, called by Genth and Gibbs *praseo-cobalt*, being sometimes formed simultaneously). The wine-yellow crystals of luteo-cobaltic sulphate contain $Co^4(SO^4)^3.12NH^3 + 5H^2O$, and give off 4 at. water in dry air, or in vacuo. According to Dana, they are trimetric combinations, $\infty P . 0P . \frac{3}{4}P . \frac{2}{3}P . 3\bar{P}\infty . \breve{P}\infty$; also with $3P\infty$ or $\infty\breve{P}\frac{3}{2} . \bar{P}\infty . 3\breve{P}\infty$; also with $0P$ and $\breve{P}\infty$. Inclination of $\infty P : \infty P$ = 113° 38′ and 66° 22′; $\infty\breve{P}\frac{3}{2} : \infty\breve{P}\frac{3}{2}$ = 88° 44′ and 91° 16′; $P\infty ; \breve{P}\infty$, on the principal axis = 112° 8′; $P\infty : \breve{P}\infty$, also on the same = 88° 22′; Luteo-cobaltic sulphate is isomorphous with the chloride, and the two salts are capable of crystallising together in all proportions.

Luteo-cobaltic chromate, obtained by precipitation (pure only from the nitrate), is yellow, soluble in hot water, and separates therefrom in yellow crystals. This salt also crystallises in all proportions with the chloride. (Gibbs and Genth.)

AMMONIO-PERCOBALTIC SALTS, or OXYCOBALTIC SALTS. **Frémy** (*loc. cit.*).—These salts contain 5 at. ammonia associated with a basic salt of dioxide of cobalt. Thus, the *nitrate* is $Co^2O^2.N^2O^5.5NH^3. + H^2O$, and the *sulphate*, $Co^2O^2.SO^3.5NH^3 + \frac{3}{2}H^2O$. They are produced by the action of the air on concentrated solutions of ammonio-cobaltous salts. They have generally an olive-brown colour; crystallise well, are but slightly soluble in the ammoniacal liquid, and are decomposed by water, especially when hot, with evolution of oxygen, liberation of ammonia, and separation of a green basic salt containing the oxide Co^3O^4. The nitrate of this group was first prepared, though not analysed, by L. Gmelin. (*Handbook*, v. 342.)

The oxycobaltic salts may be supposed to contain the diatomic base, Co^2O, thus:

$$\text{The } \textit{nitrate} = \left.\begin{matrix}(NO^2)^2\\(Co^2O)''\end{matrix}\right\}O^2.5NH^3.$$

$$\text{The } \textit{sulphate} = \left.\begin{matrix}(SO^2)''\\(Co^2O)''\end{matrix}\right\}O^2.5NH^3.$$

General formulæ of the Ammoniacal Cobalt-compounds.—These compounds may be represented as ammonium-salts, in which part of the hydrogen in one or more molecules of NH^4 is replaced by ammonium itself, and another portion, in the ammonio-cobaltous salts, by the monatomic radicle Co' = 29·5; in the ammonio-cobaltic salts by the triatomic radicle Cco''' = Co^2 = 59; and in the ammonio-percobaltic salts, by the diatomic radicle $(CcoO)''$ = 75. Such formulæ have been proposed by Weltzien (Ann. Ch. Pharm. xcvii. 19), and H. Schiff (Compt. rend. liii. 411).

In the following formulæ, which are nearly the same as those of Schiff, the symbol Am stands for NH^4 and X for a monatomic acid radicle, such as nitryl, NO^2.

α. Diammonio-cobaltous salts . . . . . = $\left.\begin{matrix}N(Co'AmH^2)\\X\end{matrix}\right\}O$

β. Triammonio-cobaltous salts . . . . . = $\left.\begin{matrix}N(Co'Am^2H)\\X\end{matrix}\right\}O$

γ. Pentammonio-percobaltic salts (oxycobaltic salts) = $\left.\begin{matrix}N^2[(CcoO)''Am^3H^3]\\X^2\end{matrix}\right\}O^2$

δ. Tetrammonio-cobaltic salts (fusco-cobaltic salts) = $\left.\begin{matrix}N^3(Cco'''AmH^8)\\X^2H\end{matrix}\right\}O^3$

ε. Pentammonio-cobaltic salts:

Diacid, or Purpureo-cobaltic . . . $\left.\begin{matrix}N^3(Cco'''Am^2H^7)\\X^2H\end{matrix}\right\}O^3$

Triacid, or Roseo-cobaltic . . . . $\left.\begin{matrix}N^3(Cco'''Am^2H^7)\\X^3\end{matrix}\right\}O^3$

ζ. Xantho-cobaltic salts . . . . . . = $\left.\begin{matrix}N^3[Cco'''Am^2H^6(NO)]\\X^2H\end{matrix}\right\}O^3$

η. Hexammonio-cobaltic salts (luteo-cobaltic salts) = $\left.\begin{matrix}N^3(Cco'''Am^3H^6)\\X^3\end{matrix}\right\}O^3$

Some of these formulæ, viz. those of the fusco-, purpureo-, and xantho-cobaltic salts, differ by 1 at. H from those previously given; but in compounds of such complexity, the question of 1 atom of hydrogen more or less can scarcely be decided by analysis.

The formulæ of the chlorides and oxychlorides are deduced from those in the table by substituting 1 or more at. Cl for a corresponding number of atoms of XO.

The salts β are transformed, by the joint action of ammonia and oxygen into γ, and these, by further oxidation, are resolved into ammonia and the salts δ, which again, by addition of 1 at. NH^3 are transformed into ϵ; and these last, by the further action of ammonia, yield η. The salts ζ are formed by the action of nitrous acid on ϵ, and are reconverted into the diacid salts ϵ, with evolution of nitric oxide, by the action of strong acids.

For Weltzien's formulæ, see *Graham's Elements of Chemistry*, 2nd edition, ii. 721. Gibbs and Genth object to the representation of these compounds as ammonium-salts, and express their composition by means of formulæ involving so-called conjugate radicles, such as $6NH^3\frown Co^2$ in the luteo-cobaltic salts, and $NO\frown 5NH^3\frown Co^2$ in the xantho-cobaltic salts. It is not easy to say what is gained by such a mode of representation.

COBALT-BLOOM. *Erythrine, Prismatic Red Cobalt, Red Cobalt-Ochre, Cobalt-mica, Kobalt-blüthe.*—A hydrated arsenate of cobalt, $Co^3AsO^4 + 4H^2O$, or $3CoO.AsO^5 + 8HO$, occurring in monoclinic crystals, in which the orthodiagonal, clinodiagonal, and principal axis are as 1·3818 : 1 : 0·9747. Inclination of clinodiagonal to principal axis = 70° 54′; $\infty P : \infty P = 111° 16'$. Observed faces $+ P\infty \,.\, + P \,.\, [\infty P \infty] \,.\, [\infty P 4] \,.\, \infty P\frac{3}{2} \,.\, \infty P \infty$ sometimes with $+ 3P\infty$ and $+ \frac{3}{2}P\infty$ between $\infty P \infty$ and $+ P\infty$. The faces $\infty P \infty$ and $+ P\infty$ are vertically striated. It is likewise found in globular and vermiform masses; also pulverulent, incrusting. Specific gravity = 2·948. Hardness, 1·5—2·5, least on $[\infty P \infty]$. Lustre on $[\infty P \infty]$ pearly; on the other faces, adamantine inclining to vitreous. Colour, red of various shades, grey and green; the red tints incline to blue when viewed at right angles to cleavage. Streak, peach-blossom red. Sectile. Flexible in thin plates.

Analyses of cobalt-bloom from Schneeberg by Karsten (Pogg. Ann. lx. 261), gave

As^2O^5	Co^2O	Fe^2O	Ca^2O	H^2O	
38·43	36·52	1·01	—	24·10	= 100·06
38·30	33·42	4·01	—	24·08	= 99·81
38·10	29·19	—	8·00	23·90	= 99·19

The formula requires 38·43 As^2O^5, 37·53 Co^2O, and 24·02 water.

The mineral, when heated in a tube, yields water and turns blue if pure, green if it contains nickel or iron. Before the blowpipe, on charcoal, it gives an arsenical odour and melts in the inner flame to a dark grey bead of arsenical cobalt; gives with fluxes the usual cobalt reaction. Dissolves easily in acids.

Earthy cobalt-bloom (*Kobalt-beschlag*), of peach-blossom colour, is arsenate of cobalt with free arsenious acid. A specimen from Schneeberg analysed by Karsten gave 51·00 per cent. As^2O^3, 19·10 As^2O^5, 16·60 Co^2O, 2·10 Fe^2O, and 11·90 water (= 100·70), with traces of nickel, lime, and sulphuric acid.

Cobalt-bloom occurs in minute crystals at Schneeberg in Saxony, Saalfeld in Thuringia, Riechelsdorf in Hessia, Wolfach and Wittichen in Baden, and Modum in Norway. The earthy varieties are found in Dauphiny, in Cornwall, and near Alston, Cumberland. A green variety occurs at Platten in Bohemia. The mineral is also found at Prince's mine, Lake Superior, in calcite. When abundant, it is used for the manufacture of smalt. (Dana, ii. 407.)

COBALT-BLUE. A pigment of a fine blue colour, like that of ultramarine, obtained by mixing the solution of a cobalt-salt, perfectly free from iron and nickel, with a solution of pure alum, precipitating with an alkaline carbonate, carefully washing the precipitate, then drying and igniting it strongly. It is a compound of protoxide of cobalt and alumina, and is used both as oil and water colour.

COBALT-GLANCE. See COBALTINE.

COBALT-GREEN. *Rinman's Green.* — A permanent green pigment prepared by precipitating a mixture of the sulphates of zinc and cobalt with carbonate of sodium, and igniting the precipitate after thorough washing; — or by mixing a solution of nitrate of cobalt with oxide or nitrate of zinc, then evaporating and igniting.

COBALTINE. *Cobalt-glance, Glance-cobalt, Silver-white cobalt, Cobalt gris.*— A native sulpharsenide of cobalt, Co^2AsS or $CoAs\,.\,CoS^2$, occurring in forms of the regular system, viz. the cube, octahedron, pentagonal dodecahedron, and several combinations of these forms. Cleavage parallel to the cubic faces. Also massive, granular or compact. Specific gravity = 6—6·3. Hardness = 5·5. Fracture imperfect, conchoïdal, uneven. Opaque, with metallic lustre. Colour silver-white, inclining to copper-red, occasionally tarnished. Streak, greyish-black. Brittle.

Before the blowpipe, it gives off fumes of arsenic, and yields, after roasting, a dull black feebly magnetic globule, which colours borax blue. It dissolves in warm nitric acid leaving a residue of arsenious acid.

Analyses.—*a*, from Skutterud by Stromeyer; *b*, from Siegen by Schnabel; *c*, from Orowitza in the Banat by Huberdt; *d*, from the same by Patera; *e*, from Skutterud by Ebbinghaus; *f*, from Siegen by Schnabel. (*Rammelsberg's Mineralchemie*, p. 60.)

	Co	Fe	As	Sb	S	
a . .	33·10	3·23	43·46	. .	20·08	= 99·88
b . .	29·77	6·38	44·75	. .	19·10	= 100·00
c . .	30·37	5·75	44·13	. .	19·75	= 100·00
d . .	32·03	4·56	43·63	. .	19·78	= 100·00
e . .	32·60	3·47	43·68	. .	20·58	= 100·34
f . .	8·67	25·98	42·53	2·84	19·98	= 100·00

The formula Co^2AsS requires 35·5 Co, 45·2 As, and 19·3 S. In analysis *f*, three-fourths of the cobalt is replaced by iron.

Cobaltine occurs in large splendid crystals at Tunaberg, Riddarhyttan, and Hokansbö in Sweden, and at Skutterud in Norway. It is also found at Querbach in Silesia, Siegen in Westphalia, and several localities in Cornwall. This species and smaltine afford the greatest part of the smalt of commerce. The most productive mines are those of Vena in Sweden. (Dana, ii. 58.)

COBALT-MICA. Syn. with COBALT-BLOOM.

COBALT-PYRITES. See COBALT, SULPHIDES OF (p. 1050).

COBALT-VITRIOL. *Bieberite, Red Cobalt, Rhodalose.*—Hydrated native sulphate of cobalt, of somewhat variable constitution, found in stalactites, and crusts investing other minerals, in the rubbish of old mines at Bieber near Hanau, and at Leogang in Salzburg. It is translucent, with flesh-red or rose-red colour and vitreous lustre. A specimen analysed by Winkelblech (Ann. Ch. Pharm. xiii. 265), after being freed by solution and filtration from admixed manganous arsenate, yielded 29·05 SO^3, 19·91 Co^2O, 3·87 Mg^2O and 46·83 water, agreeing nearly with the formula $(Co^6Mg^2).(SO^4)^4. + 28\,aq.$

COBALT-YELLOW. This compound, discovered by Saint-Èvre in 1852 (Ann. Ch. Phys. [3] xxxviii. 177), and further examined by A. Stromeyer (Ann. Ch. Pharm. xcvi, 218), is produced by the action of nitrite of potassium on cobaltous salts. Saint-Èvre regards it as a compound of peroxide of nitrogen with cobaltous oxide and potash, $CoO.KO.2NO^4$ or $CoKO.(NO^2)^2$:

$$\underset{\text{Nitrate of cobalt.}}{CoNO^3} + \underset{\text{Nitric acid.}}{2HNO^3} + \underset{\text{Nitrite of potassium.}}{4KNO^2} = \underset{\text{Cobalt-yellow.}}{CoKO.(NO^2)^2} + \underset{\text{Nitrate of potassium.}}{3KNO^3} + \underset{\text{Nitric oxide.}}{2NO} + H^2O$$

Stromeyer on the other hand regards it as a basic potassio-cobaltic nitrite, $Co^2O^3.3KO.5NO^3$, or $\left.\begin{matrix}(NO)^{10}\\(Cco''')^2.K^6\end{matrix}\right\}O^{11}$, on which supposition its formation may be represented by the equation:

$$4\underset{\text{Nitrate of cobalt.}}{\left(\left.\begin{matrix}NO^2\\Co\end{matrix}\right\}O\right)} + 10\underset{\text{Nitrite of potassium.}}{\left(\left.\begin{matrix}NO\\K\end{matrix}\right\}O\right)} + O = \underset{\text{Cobalt-yellow.}}{\left.\begin{matrix}(NO)^{10}\\(Cco''')^2.K^6\end{matrix}\right\}O^{11}} + 4\underset{\text{Nitrate of potassium.}}{\left(\left.\begin{matrix}NO^2\\K\end{matrix}\right\}O\right)}$$

The compound is prepared: 1. By adding an alkaline solution of nitrite of potassium (obtained by passing the nitrous vapours evolved from a mixture of nitrate of potassium and starch into caustic potash) to an acid solution of nitrate of cobalt.—2. By adding potash, not in excess, to a solution of nitrate of cobalt, so as to throw down a blue basic salt (p. 1043), treating this with a slight excess of nitrite of potassium, and adding nitric acid in a thin stream from a pipette.—3. By treating nitrate of cobalt with a slight excess of potash, so as to throw down the rose-coloured hydrate, and passing nitric oxide gas into the mixture.—It forms a bright yellow crystalline powder composed of microscopic four-sided needles with pyramidal summits. It is insoluble in cold water, also in alcohol and ether, but when boiled with water, it gradually dissolves, with evolution of acid vapours, and the solution, if subsequently evaporated, yields a lemon-yellow salt of different composition. Nitric acid and hydrochloric acid do not act upon it in the cold, but decompose it at the boiling heat, with evolution of nitrous vapours. Sulphydric acid decomposes it very slowly, sulphide of ammonium immediately forming black sulphide of cobalt; when heated, it assumes an orange-yellow colour, gives off water and afterwards nitrous fumes, and leaves sesquioxide of cobalt mixed with nitrate of potassium.

Cobalt-yellow forms an excellent pigment for artistic purposes, having a beautiful colour, like that of sulphide of cadmium, great permanence, and mixing easily with other colours. Its formation affords also an excellent method of separating cobalt from other metals, especially from nickel (p. 1046).

When a solution of lead is mixed with nitrite of potassium and acetic acid, the liquid assumes a yellow colour, but no precipitation takes place; but on adding a cobalt-salt, a yellowish-green precipitate (brownish-black and crystalline from dilute solutions) is formed, whose composition is that of the yellow cobalt-compound, having half the potassium replaced by lead. (Stromeyer.)

COCA. The leaves of *Erythroxylon Coca*, a plant cultivated in the mountainous districts of Peru and Bolivia, and in some parts of Brazil, are extensively used by the inhabitants of those countries, and of other parts of South America, for chewing like tobacco, for which purpose they are mixed with burnt lime, or the ash of a peculiar plant, the *Chenopodium Quinoa*, according to Niemann. They possess powerful tonic and sedative properties, and the practice of chewing them is said to give great power of enduring fatigue, even on a scanty supply of food; but like the use of opium, it is apt to become an indispensable necessity, and ultimately produces all the baneful effects of a narcotic poison, such as hallucinations and premature decay both of body and of mind. The use of coca is said to prevail among ten millions of people in South America, the annual consumption amounting to thirty million pounds of the dry leaves. Coca leaves do not long retain their activity; indeed they are said to become useless after a year's keeping.

Coca leaves contain, according to Niemann (Arch. Pharm. [2] ciii. 120 and 291), a crystallisable basic substance called cocaïne, a volatile odoriferous substance, a peculiar tannic acid, cocatannic acid, and a waxy body, coca-wax.

The volatile constituent of coca leaves has a strong tarry, almost intoxicating odour. On distilling the leaves with water a slightly turbid distillate is obtained, from which no oil separates; but on saturating it with common salt and redistilling, a very small quantity of a white non-crystalline substance is obtained, which is volatile, fusible, lighter than water, and possesses in a very high degree the odour of the leaves.

Cocatannic acid remains in the aqueous decoction of the leaves after the cocaïne has been precipitated by carbonate of sodium, and is left as a brown-red amorphous substance when the liquid is evaporated. Its solution is coloured deep brownish-green by ferric chloride, and is precipitated by tartar emetic, or solution of white of egg, but not by gelatin; it reduces chloride of gold even in the cold.

Coca-wax is contained in the precipitate formed by lime in extract of coca leaves prepared with alcoholic sulphuric acid. It contains 80·2 per cent. carbon and 13·4 hydrogen, agreeing with the formula $C^{50}H^{50}O^{3}$, and with the composition of the wax from grass, and of that from *Syringa*, as determined by Mulder. If the precipitate be exhausted with ether, the ether evaporated, and the residue repeatedly boiled with alcohol, the solution on cooling deposits a wax, which is white, amorphous, very friable, and becomes strongly electric by trituration. It is insoluble in water, dissolves slowly in boiling alcohol, easily in ether, sometimes, though rarely, remaining in a somewhat crystalline form when the ethereal solution is evaporated. It melts at 70° C., and decomposes when heated. Aqueous alkalis do not act upon it, but melting hydrate of potassium decomposes and dissolves it.

The substance mixed with coca leaves, to render them fit for chewing, is called *Llipta*. According to Niemann, it is the ash of *Chenopodium Quinoa*. Gädeke found it in 40·0 K^2O, 17·7 Na^2O, 5·6 Mg^2O, 0·2 Fe, 4·5 P^2O^5, 1·8 SO^3, 2·5 Cl, 6·7 SiO^2, 3·0 CO^2, 13·5 sand, 1·0 water, and a trace of organic matter. (Handw. d. Chem. ii. [2] 123.)

COCAÏNE. $C^{16}H^{19}NO^{4}$ or $C^{32}H^{19}NO^{8}$. (Niemann, Ann. Ch. Pharm. cxiv. 213.) —An alkaloïd obtained from coca leaves, resembling atropine in many of its properties. Niemann assigns to it the formula $C^{32}H^{20}NO^{8}$; but this is improbable, because the sum of the atoms of H and N is an odd number.

Cocaïne is prepared by digesting coca leaves with 85 per cent. alcohol containing a small quantity of sulphuric acid, mixing the expressed mass with milk of lime, neutralising the filtrate with sulphuric acid, evaporating off the alcohol, mixing the residue with water, precipitating the resulting yellow-brown solution with carbonate of sodium, treating the brown precipitate of impure cocaïne with ether, and evaporating. Cocaïne then remains, partly amorphous, partly crystalline, and may be purified by repeated treatment with alcohol.

Cocaïne crystallises in small, colourless, inodorous prisms; it has a slightly bitter taste, and produces temporary insensibility on the part of the tongue with which it comes in contact. It is soluble in 704 pts. of water at 12° C., more soluble in alcohol, and still more in ether. It melts at 98° C., and solidifies to a transparent mass, which gradually becomes white and crystalline. At a higher temperature, a very small portion appears to volatilise undecomposed, but the greater part is decomposed, yielding ammoniacal products. Cocaïne dissolves without colour in strong nitric, hydrochloric, and sulphuric acid, the last solution only becoming black when heated.

Cocaïne is strongly alkaline; it dissolves in dilute acids, and neutralises them completely. Its salts do not crystallise readily, the hydrochlorate, however, more easily than the others. Solutions of cocaïne-salts yield with *caustic alkalis*, a white precipitate soluble only in a large excess of fixed alkali, more soluble in ammonia. *Carbonate of sodium* forms a precipitate insoluble in excess. *Carbonate of ammonium* a precipitate easily soluble in excess. *Acid carbonate of potassium* and *phosphate of sodium* produce a red precipitate. *Sulphocyanide of potassium* produces but a slight turbidity; *picric acid* forms a sulphur-yellow precipitate, which gradually aggregates into resinous lumps; *tannic acid*, on addition of hydrochloric acid, forms a white precipitate, which aggregates in a similar manner; *mercuric chloride* and *potassio-mercuric iodide* produces white precipitates; *iodine-water* a kermes-brown; *iodide of potassium* containing iodine, a dark-brown precipitate; *trichloride of gold* and *dichloride of platinum* yield precipitates with the hydrochlorate; *protochloride of tin* produces a white precipitate, even in slightly acid and dilute solutions.

In most of these reactions, cocaïne closely resembles atropine (i. 474); the latter, however, is not precipitated by carbonate of ammonia, or in acid solutions by stannous chloride; the two bases differ also in their reactions with gold and platinum-salts, and in their melting points, that of cocaïne being 6° C. higher than that of atropine.

Hydrochlorate of Cocaïne crystallises in white slender needles, easily soluble in water; it has a bitter taste and produces on the tongue the peculiar action of the base itself, but in a higher degree. The solution, even when very dilute, is precipitated by *chloride of gold*, yielding the compound $C^{16}H^{19}NO^4.HCl.AuCl^3$, which crystallises from alcohol in gold-yellow scales or laminæ. This gold-salt melts when heated, and then yields a sublimate of benzoic acid, affording a very characteristic reaction. The *chloroplatinate* is a yellow-brown flocculent precipitate, which soon becomes crystalline, and is nearly insoluble in hydrochloric acid.

Acetate of Cocaïne crystallises readily; the *nitrate* with difficulty. The *sulphate* remains when its solution is evaporated, as a colourless varnish-like mass, which becomes crystalline after a while; it is permanent in the air.

COCATANNIC ACID.—COCA-WAX. See COCA (p. 1059).

COCCIN. A peculiar nitrogenous substance existing, according to Pelletier and Caventou, in cochineal, and forming, as it were, the flesh of the insect; it resembles gelatin in some of its characters, albumin and fibrin in others.

COCCINITE. Haidinger's name for the reddish-brown mineral, with adamantine lustre, from Casas Viejas in Mexico, which Del Rio regards as mercuric iodide. It melts and sublimes with facility.

COCCINNIC ACID. A volatile fatty acid existing, according to Pelletier and Caventou, in cochineal.

COCCINONIC ACID. A derivative of euxanthic acid (p. 712).

COCCODEA VIRIDIS. This plant contains a green colouring matter differing from chlorophyll. (Salm-Horstmar, Pogg. Ann. xciv. 466; cxv. 176.)

COCCOGNIC ACID. An acid contained, according to Göbel (Buchn. Repert. viii. 203), in the seeds of *Daphne Gnidium.* It is dissolved by water from the alcoholic extract; crystallises in colourless, slightly acid prisms; does not precipitate lime-water, or the solutions of chloride of barium, acetate of lead, or ferrous sulphate.

COCCOLITE. A name applied to certain granular varieties of augite.

COCCOLOBA UVIFERA. The plant which yields American kino.

COCCULIN. Syn. with PICROTOXIN.

COCCULUS INDICUS. *Graine of Paradise.*—The fruit of the *Cocculus suberosus* (Dec.), *Menispermum cocculus* (Linn.), *Anamirta cocculus* (Wight and Arnott). It possesses strong narcotic and poisonous properties, due to the presence of a bitter substance, picrotoxin ($C^5H^6O^2$), of which it contains about $\frac{1}{50}$ of its weight. It is used to adulterate beer, and is sometimes thrown into water to intoxicate or kill fish; it is occasionally employed in medicine. (See *Ure's Dictionary of Arts, Manufactures and Mines*, i. 786; also the article BEER in this Dictionary, i. 537.)

COCCUSIC ACID, $C^8H^8O^5$, is the acid corresponding to nitrococcusic acid, a product of the action of nitric acid on carmine (i. 804); it has not yet been obtained in the separate state.

COCHINEAL. *Cochenille, Coccionella.*—Several insects of the genus *Coccus*, especially the *Coccus cacti* or cochineal insect, yield a splendid colouring matter, extensively used for dyeing and the preparation of pigments. The cochineal insect lives on various plants of the genus *Opuntia*, especially on the nopal, *Opuntia decumana*, *O. cactus*, and *O. monacantha*. It is a native of Mexico, but its cultivation has been introduced into many other hot countries, namely, the West Indies, Teneriffe, Madeira, Algeria, Java: in colder climates it does not thrive. The female insects only are collected; they are killed either by drying in the sun, on hot plates, or in stoves, or by immersing them for a short time in hot water. The last method yields a cochineal of somewhat red-brown aspect, whereas if the insects have been killed by drying, it has more of a blackish or ash-grey colour, with a silvery surface; the latter is preferred. The dry cochineal is freed from dust and adhering impurity by shaking it in sacks; the fine dust is then removed by sifting, and the larger and smaller lumps in the remaining mass are separately sorted.

Other species of coccus probably contain the same colouring matter, but in smaller quantity and more contaminated with foreign substances.

Cochineal occurs in commerce in nearly egg-shaped grains 1 or 2 lines long, somewhat hollowed below and arched above, about 70,000 going to the pound. It is inodorous, very friable, and contains within it a dark red granular mass, which yields a powder of a fine deep red colour; it has a bitter, slightly astringent taste, and leaves but a small quantity of ash when burnt. In water, it swells up considerably, the shape of the insect and its three pairs of legs then becoming distinctly visible.

The first investigation of cochineal was made by John (*Chemical Tables*, p. 127), who found in it 50 per cent. coccus-red (carmine), 10 waxy fat, 1·5 inorganic salts (chlorides of potassium and ammonium, and phosphates of calcium, iron, and magnesium), 28·0 animal matter, and 10·5 water. According to Pelletier and Caventou (Ann. Ch. Phys. vii. 90; viii. 255), it contains a peculiar nitrogenous matter, coccin (p. 54), which forms, as it were, the flesh of the insect, and an acid, not examined, to which they give the name of coccinic acid.

The colouring matter of cochineal is carminic acid (i. 804).

The watery extract likewise contains a crystallisable nitrogenous substance, $C^9H^{11}NO^3$, homologous with tyrosine, ($C^8H^9NO^3$), and very similar to it in appearance and reactions. It remains in the aqueous decoction of cochineal after the carminic acid has been precipitated by acidulated acetate of lead, and may be separated by removing the excess of lead from the filtrate with sulphuretted hydrogen, and evaporating to a syrup; it then separates in a crystalline mass, and an additional quantity may be obtained by further concentration. It is insoluble in alcohol and ether, soluble without decomposition in hydrochloric acid, decomposed by strong nitric acid, the liquid yielding crystals of a new acid on evaporation; hot nitric acid produces a more thorough decomposition, with separation of charcoal. The chalky substance dissolves in alkalis, and is separated therefrom by acids. It does not appear to form definite compounds either with acids or with bases.

The mother-liquor from which the whole of the chalky substance has been removed, dries up to a soft mass amounting to 10 or 12 per cent. of the cochineal; part of this mass is soluble in alcohol, the remainder in water.

Cochineal boiled with water yields a deep red liquid, which assumes a reddish-yellow colour when mixed with *tincture of galls* or with strong *acids*, and a beautiful violet with *lime-water;* it is precipitated violet-blue by *neutral acetate of lead*, bright red by *ammonia*, dark black-brown by *ferric chloride;* olive-green by a larger quantity, deep red by *alum*. After the cochineal has been thoroughly boiled with water, a brownish animal substance remains.

The red colour of cochineal is likewise extracted by alcohol.

The chief use of cochineal is for the preparation of carmine and carmine-lakes (i. 804). It is likewise employed for dyeing wool and silk scarlet (the fabric being steeped first in annotto, then in a decoction of cochineal containing cream of tartar and stannoso-stannic chloride), or crimson (cochineal with tartar and tin-salt). Cochineal is likewise used for the preparation of rouge, of painters' colours, and of red ink, and for colouring tooth-powder, confectionery, liqueurs, &c.

Cochineal varies much in colouring power, according to its source and mode of preparation. The relative quantities of colouring matter in different samples may be estimated approximately by the depth of colour of a solution obtained by heating 1 gramme of cochineal in the water-bath for an hour, with 1000 grammes of water and 20 drops of a saturated solution of alum; also by the depth of colour which the same extract will impart to wool. Robiquet estimated the amount of colouring matter by means of a graduated solution of chlorine; Anthon by a graduated solution of an alumina-salt.

A better method is that of Penny, depending on the action of ferricyanide of potassium. 1 gramme of cochineal is extracted with 50 cub. cent. of dilute potash-solution: the extract is further diluted with 100 cc. of cold water; and the purple solution thereby obtained is mixed, when cold, with a graduated solution of ferricyanide of potassium (1 grm. of the salt to 200 cc. of solution), till its colour changes to dark brown. All these methods yield only relative results for comparing different sorts of cochineal one with the other. (See *Ure's Dictionary of Arts, Manufactures and Mines*, i. 786; Handw. d. Chem. 2te Aufl. ii. [2] 127.)

COCHINEAL-RED is properly carmine; the same term is, however, applied to a splendid red artificial colour, which contains a considerable quantity of arsenate of aluminium, and is therefore highly poisonous.

COCHLEARIA. A genus of cruciferous plants, including horse-radish and scurvy-grass, distinguished by their acridity, arising from the presence of volatile oils, similar to, or identical with, volatile oil of mustard (sulphocyanate of allyl).

Cochlearia Armoracia. Horse-radish.—The volatile oil of this plant, when purified, is identical with oil of mustard. It appears to exist in the root ready formed, and may be obtained by bruising the root to a pulp, and distilling it *per se.* The best mode of preparation, however, is to distil 3 pts. of the finely chopped root with 2 pts. water, in a glass vessel (if a copper still be used, only a small quantity of oil is obtained, in consequence of the formation of metallic sulphide). 100 pts. of the root thus treated yield about 0·05 pt. of crude oil, which may be purified by rectification with water and drying over chloride of calcium. The purified oil is colourless or pale yellow; has a density of 1·01; smells like oil of mustard, and contains 48·41 per. cent. C, and 5·26 H (sulphocyanate of allyl, $C^3H^5.CNS$, requires 48·49 C and 5·05 H). The crude oil is light yellow, of the consistence of cinnamon-oil, heavier than water, evaporates quickly, has an intolerable odour of horse-radish, tastes sweet at first, afterwards sharp and burning, and inflames the lips and tongue. When kept under water for a year, it disappears, and silvery needles are formed, which smell like horse-radish, excite irritation in the throat, melt and volatilise when heated, and dissolve but slowly in alcohol. Oil of horse-radish is decomposed by nitric acid, sulphuric acid, and chlorine. It yields sinapoline with oxide of lead, and thiosinnamine with ammonia. It dissolves slightly in water, the solution forming a brown precipitate with acetate of lead, black with nitrate of silver. It dissolves readily in alcohol. (Gm. x. 55).

Cochlearia officinalis. Common scurvy grass.—The herb of this plant contains 92·2 per cent. water, and yields 1·6 per cent. ash, which, according to Geiseler, is very rich in potash, but, according to Braconnot, contains soda. The base is partly combined with nitric acid and, according to Braconnot, with an organic acid resembling malic acid.

Oil of scurvy-grass, *Oleum cochleariæ*, obtained by distilling the herb with water, is yellow, pungent, of specific gravity 0·942 (Geiseler), boils between 156° and 159° C. (Simon). It dissolves easily in alcohol, and the alcoholic solution, *Spiritus cochleariæ*, may be obtained by distilling the bruised herb with alcohol. According to Geiseler (Arch. Pharm. cxlvii. 136, 257), the oil is an oxysulphide of allyl, C^6H^5SO, and yields with ammonia a crystalline compound, $C^6H^5SO.NH^3$. [These formulæ are doubtful.] The oil does not exist ready formed in the plant, but is produced by the action of myrosin in presence of water, on a peculiar substance existing therein. According to Winckler (Jahrb. pr. Pharm. xviii. 319), this substance is neutral, and is converted into the volatile oil by the joint action of myrosin and lime.

Scurvy-grass camphor, or Cochlearin, $C^6H^7O^2$(?), is a crystalline substance sometimes deposited from *Spiritus cochleariæ*, and from the water which has been distilled off the plant. It forms small, nacreous, shining laminæ or needles, having a faint odour, and sharp aromatic taste. Specific gravity = 1·248. It melts at 45° C., sublimes without alteration, dissolves lightly in pure water, easily in water containing carbonate of potassium, also in alcohol and ether. (Maurach, Repert. Pharm. xcix. 128.)

Cochlearia Draba, Whitlow Pepperwort, yields, by distillation with water, a volatile oil, similar to that obtained from radish-seeds. (Ploss, Ann. Ch. Pharm. lviii. 40.)

Cochlearia anglica. English scurvy-grass.—The fresh herb of this plant contains, according to T. J. Herapath (Chem. Soc. Qu. J. ii. 4), 2·42 per cent. ash; the dry herb 21·1 per cent. ash; of which 78·1 per cent. are soluble, and 21·9 per cent. insoluble in water. 100 parts of the ash contain:

Soluble in Water.		*Insoluble in Water.*	
Potash	0·1	Carbonate of calcium	7·2
Soda	7·7	Carbonate of magnesium	1·3
Carbonic acid (CO^2)	3·6	Phosphate of calcium	10·3
Sulphuric acid (SO^3)	3·1	Ferric phosphate	0·6
Chloride of sodium	63·6	Silica	2·5

COCHLEARIN. See COCHLEARIA OFFICINALIS.

COCINIC ACID. *Cocostearic acid. Cocylic acid. Coconustalgsäure.*—A fatty acid, or probably a mixture of acids, obtained from cocoa-nut oil.

Bromeis (Ann. Ch. Pharm. xxxv. 277), by saponifying cocoa-nut fat, decomposing the soap with an acid in the usual way, pressing the resulting fatty acid between paper, and recrystallising from alcohol, obtained a nearly inodorous fatty acid, which melted at 35° C., solidified to a porcelain-like mass translucent at the edges, and distilled without decomposition. Saint-Èvre (Ann. Ch. Phys. [3] xx. 95) decomposes the soda-soap of cocoa-nut oil with acetate of lead; exhausts the lead-soap with ether; decomposes the undissolved soap with an acid; and crystallises the fatty acid from alcohol. From a saturated solution in aqueous alcohol, it crystallises, on cooling, in needles; but from a solution in strong alcohol, by evaporation, in amorphous masses. It melts at 34·5° C., and volatilises without decomposition only in a stream of gas.

Bromeis assigned to his cocinic acid the formula $C^{27}H^{27}O^4$, but his analysis, calculated according to the more recently determined atomic weight of carbon ($C = 6$), gives rather $C^{26}H^{26}O^4$, or $C^{13}H^{26}O^2$. Heintz has since announced the separation of an acid of the same composition from spermaceti. Fehling obtained from cocoa-nut oil an acid resembling the acid prepared by Bromeis in appearance and melting point, and corresponding exactly to the formula $C^{13}H^{26}O^2$.

Saint-Èvre, on the other hand, assigned to the cocinic acid which he obtained, the formula $C^{11}H^{22}O^2$, though it agrees very closely with that of Bromeis in the melting point.

Heintz regards the acid $C^{13}H^{26}O^2$ from cocoa-nut oil, and likewise that obtained by himself from spermaceti, as a mixture, especially on account of its melting point, which is lower than that of lauric acid ($C^{12}H^{24}O^2$); whereas if it were really a definite acid, its melting point would be intermediate between those of lauric acid (44° C.) and myristic acid, $C^{14}H^{28}O^2$ (54° C.). He finds, indeed, that a mixture of 14 pts. lauric and 2 pts. myristic acid melts at about 35° C. Saint-Èvre's formula, $C^{11}H^{22}O^2$, is on this account more probable.

Cocinate of barium, crystallised from boiling alcohol, is, according to Bromeis, $C^{13}H^{25}BaO^2$. *Cocinate of silver*, $C^{13}H^{25}AgO^2$ (Bromeis), $C^{11}H^{21}AgO^2$ (Saint-Èvre), is obtained by precipitation from alcoholic solutions, in white flocks melting at 55° C., soluble in ether, sparingly soluble in alcohol.

Cocinate of ethyl, $C^{13}H^{25}(C^2H^5)O^2$ or $C^{11}H^{21}(C^2H^5)O^2$, obtained by passing hydrochloric acid gas into a hot alcoholic solution of cocinic acid, washing the product with weak alkali, and drying over chloride of calcium, is a liquid having a faint-yellow colour, a very pungent odour of apples, and a sweet mawkish taste.

COCININ. *Cocinate of glyceryl.*—The name of the neutral fat corresponding to cocinic acid. The separate identity of such a fat, like that of the acid itself, must, for the present be considered doubtful. Brandes (Ann. Ch. Pharm. xv. 115), by expressing the fat from cocoa-nuts, and crystallising it repeatedly from boiling alcohol, obtained a snow-white laminar crystalline fat, of specific gravity 0·92 at 8° C., less soluble in pure than in common ether, soluble in 40 pts. absolute alcohol at 20° C., about 12 pts. at 44° C., sparingly soluble in aqueous alcohol of 0·75 in the cold, more soluble in the same when warm; crystallising on cooling; decomposed by dry distillation.

COCINONE. A product of the decomposition of neutral cocinate of calcium, consisting, according to Delffs (Pogg. Ann. lxxxvi. 587), of $C^{21}H^{42}O$, and therefore the acetone of Saint-Èvre's cocinic acid $C^{11}H^{22}O^2$. When purified by recrystallisation from boiling alcohol, it forms colourless, inodorous, tasteless laminæ, melting at 38° C., and boiling at a temperature beyond the range of the mercurial thermometer.

COCOA-NUT OIL. This oil or fat is obtained by pressure from the fruit of certain cocoa-palms, *Cocos nucifera*, *C. butyracea*, &c., and is imported in large quantities into Europe for the manufacture of soap. It is whitish, of unctuous consistence, with a peculiar disagreeable odour of volatile fatty acids, and a mild taste; it melts at 20° C., dissolves with aid of heat in alcohol and ether, readily in oils, both fixed and volatile, benzene, &c.

Cocoa-nut oil quickly becomes rancid, and is easily saponified. It is a mixture of several glycerides, containing also free fatty acids. By saponification it yields both fixed and volatile fatty acids. The volatile acids, which may be separated by distilling the mixture of free fatty acids with water, consist chiefly of caprylic acid mixed with small quantities of caproic and capric acids. The fixed fatty acids of cocoa-nut oil are partly liquid at ordinary temperatures, partly solid. The former have not been particularly examined; of the latter, several may be isolated by crystallisation from alcohol, viz. lauric acid, $C^{12}H^{24}O^2$, which may be obtained pure, with the melting point 43° C., by fractional precipitation of the soda soap (Oudemans, J. pr. Chem.

lxxxi. 367); the acid, $C^{11}H^{22}O^2$, which was obtained from the oil by Saint-Évre, and $C^{13}H^{26}O^2$ by **Bromeis**, (see COCINIC ACID, p. 57); **myristic acid**, $C^{14}H^{28}O^2$, likewise exists in considerable quantity in cocoa-nut oil. The acid actually obtained had very nearly the composition of myristic acid, and melted at 49° C., the melting point of the pure acid being 53·8° (**Fehling**, Ann. Ch. Pharm. liii. 399). **Görgey** (*ibid.* civ. 25) likewise found a fatty acid, $C^{15}H^{30}O^2$, melting at 56° C., which, from the examination of the silver-salt, he regarded as a mixture of myristic and palmitic acids. Fehling also found pure **palmitic acid**. **Stearic acid** is probably present in small quantity.

The solid fats of cocoa-nut oil are separated from the more liquid fats by pressure, and used for the manufacture of candles.

The solid fatty acids of cocoa-nut oil are converted, by prolonged treatment with nitric acid, into a mixture of acids of the series $C^nH^{2n-4}O^4$, viz. anchoic, suberic, pimelic, adipic, succinic acid, and an oily mass containing nitrocapric and nitrocaprylic acids.

CODEINE. $C^{18}H^{21}NO^3 + H^2O$ or $C^{36}H^{21}NO^6 + 2HO$.—A non-volatile organic base contained in opium. It was discovered by **Robiquet** in 1832 (Ann. Ch. Phys. [2] li. 259), and has been further examined by **Couerbe** (*ibid.* lix. 158), **Regnault** (*ibid.* lxviii. 136), **Gregory** (Ann. Ch. Pharm. xxvi. 44), **Will** (*ibid.* 44), **Gerhardt** (Rev. Scient. x. 203; *Traité*, iv. 40), and especially by **Anderson** (Ed. Phil. Trans. xx. [1] 57).

Preparation.—1. The aqueous infusion of opium, evaporated to a syrup, is mixed with solution of chloride of calcium; the mass is diluted with water; the resulting meconate of calcium is separated, washed several times with small quantities of water and pressed; and the liquid thus obtained is evaporated, lumps of marble being thrown into it to neutralise the free acid. Fresh quantities of meconate of calcium then separate, and the decanted liquid, if left at rest, deposits crystals of hydrochlorate of morphine and hydrochlorate of codeine. These crystals are dissolved in water, and the solution, after purification with animal charcoal, is precipitated by ammonia, which separates the greater part of the morphine, leaving the codeine in solution. The filtered liquid is evaporated over the water-bath to expel the excess of ammonia, the morphine salt remaining in solution being at the same time precipitated; the saline solution is concentrated and precipitated by caustic potash; and the precipitate of codeine is washed, dried, and dissolved in ether, whence it is deposited in crystals. (**Robiquet.**)

2. To obtain the whole of the codeine from the mother-liquor which remains after the morphine has been removed by precipitation with ammonia, as just described, it is necessary to get rid of the sal-ammoniac with which it is mixed. This may be effected by repeatedly concentrating the liquid—the greater part of the hydrochlorate of codeine then separating out, while the sal-ammoniac remains dissolved—and decomposing the remaining sal-ammoniac with caustic potash. By repeating the crystallisation a certain number of times, the hydrochlorate of codeine might be obtained quite free from sal-ammoniac; this, however, would occasion the loss of a considerable quantity of codeine, inasmuch as the two hydrochlorates do not differ greatly in solubility; but if the crystallisation be discontinued at an earlier stage, the greater part of the sal-ammoniac may be removed without loss of codeine. The crystals of hydrochlorate of codeine are then to be dissolved in boiling water, and a strong solution of caustic potash added in excess, which will precipitate the codeine, partly as an oil which gradually solidifies, partly in the crystalline state as the liquid cools. The mother-liquor yields by evaporation a fresh crop of crystals of codeine, and lastly, after reduction to a very small bulk, it becomes filled, on cooling, with long silky needles of morphine, which had been retained in solution by the excess of potash. (**Anderson.**)

3. Opium is exhausted with cold water, the morphine precipitated by ammonia, the meconic acid by chloride of calcium, and the colouring matter by subacetate of lead. The liquid filtered from the lead-precipitate is freed from lead by sulphuric acid and filtered again; the filtrate is mixed with excess of potash; the mixture left to stand in the air till carbonate of potassium has formed; and the whole agitated with ether, which extracts the codeine. (**Winckler**, Répert. Pharm. xliv. 459.)

4. **Merck** (Ann. Ch. Pharm. xi. 279) precipitates the mixture of the hydrochlorates of codeine and morphine with pure soda; treats the precipitate with cold alcohol; saturates the alcoholic solution with sulphuric acid; removes the alcohol by distillation, and adds cold water to the remaining liquid as long as it produces turbidity; then filters, evaporates to a syrup, and agitates the residue with excess of potash and with ether. The codeine dissolves in the ether and is deposited by spontaneous evaporation; it is finally treated with alcohol, to free it from an oily substance which prevents crystallisation.

Purification.—Impure crystals of codeine are purified by dissolving them in hydrochloric acid, boiling with animal charcoal, reprecipitating with caustic potash and finally dissolving the precipitate in ether containing water, in order to free the codeine from the last trace of morphine; the ether used must, however, be free from alcohol, otherwise a syrupy liquid remains, on evaporation, which cannot be made to crystallise. If anhydrous ether be used, the codeine dissolves much more slowly (Handw. d. Chem. ii. [3] 136). 100 pounds of opium yield from 6 to 8 oz. of codeine (Robiquet). The proportion of codeine in opium is from $\frac{1}{30}$ to $\frac{1}{18}$ of that of the morphine. (Anderson.)

Properties.—Codeine crystallises from anhydrous ether in small anhydrous rectangular octahedrons, truncated and modified in various ways. From hydrated ether or alcohol, and from water, it separates in hydrated crystals of the trimetric system. Those deposited from alcohol exhibit the combination $\infty P \,.\, 0P \,.\, \bar{P}\infty \,.\, \breve{P}\infty$; those from water, the combination $\infty P \,.\, \breve{P}\infty \,.\, \frac{1}{2}\breve{P}\infty$. Inclination of $\infty P : \infty P = 87° 40'$; $\bar{P}\infty : 0P = 141° 37'$; $\breve{P}\infty : 0P = 140° 23'$; $\frac{1}{2}\breve{P}\infty : 0P = 157° 25'$. Cleavage parallel to 0P. (Kopp, *Krystallographie*, 266.)

Codeine dissolves in water much more readily than morphine, especially in boiling water. 100 pts. of water at 15° C. dissolve 1·26 pts. codeine. When heated with a quantity of water less than sufficient to dissolve it, it melts to an oily mass, which remains at the bottom of the liquid. It dissolves easily in alcohol and hydrated ether, less easily in anhydrous ether. The alcoholic solution deflects the plane of polarisation of a luminous ray strongly to the left; $[\alpha] = -118·2°$; acids have scarcely any effect on the rotatory power.

Codeine is quite insoluble in potash; it dissolves in ammonia, but not to a greater extent than in pure water.

Anhydrous codeine contains:

	Calculated.		Robiquet.	Couerbe. (*mean.*)	Regnault.	Gregory. (*mean.*)	Will.	Anderson. (*mean.*)
C^{18}	216	72·24	70·36	71·84	73·31	73·05	73·27	72·01
H^{21}	21	7·02	7·58	7·37	7·19	7·21	7·25	7·09
N	14	4·68	5·35	—	4·89	4·89	—	4·50
O^3	48	16·06	—	—	—	—	—	—
	299	100·00						

The hydrated crystals contain, according to Gerhardt's analysis, 67·82 per cent. C, and 7·46 H, agreeing nearly with the formula $C^{18}H^{21}NO^3 + H^2O$, which requires 68·13 C, 7·25 H, 4·41 N, and 20·21 O.

Codeine is a strong base, quickly restoring the blue colour of reddened litmus, and precipitating the salts of lead, iron, copper, cobalt, nickel, &c.

In its action on the animal economy, codeine resembles morphine in many respects. According to Robiquet, doses of 0·02 to 0·03 grm. produce in 24 hours, especially in excitable persons, a sensation of comfort and repose, and a refreshing sleep, whereas doses of 0·15 to 0·12 grm. produce heavy sleep, with a feeling of intoxication after waking—sometimes also nausea and vomiting; more than 0·2 grm. cannot be taken in 24 hours without danger of serious consequences.

Codeine is said to be sometimes adulterated with sugar-candy; this impurity may be detected by its greater solubility in water, its smaller solubility in alcohol, and its very different action on polarised light. According to Robiquet, a solution of 0·500 grm. pure codeine in 100 cub. cent. alcohol of at least 56 per cent. gives, for the transition tint, a deflection of 11° to the left.

Decompositions.—1. When codeine is dissolved in excess of *sulphuric acid* of medium strength, and the solution is digested in a sand-bath, it acquires a dark colour, and after a while yields a precipitate with carbonate of sodium, which is not the case with codeine-salts in their ordinary state. The precipitate thus formed consists of amorphous codeine, which, after washing with water, solution in alcohol, and precipitation by water, forms a grey powder with more or less green reflection, insoluble in water, easily soluble in alcohol, and precipitated therefrom by ether. It melts at 100° C. to a black resinous mass. It dissolves easily in acids, forming amorphous salts, which dry up by evaporation to brown resins. If the action of the sulphuric acid on the codeine be prolonged, a dark green substance is obtained.

2. *Nitric acid*, according to its degree of concentration, forms with codeine either a basylous nitro-compound (p. 1067), or a yellow resin soluble in alkalis.

3. *Chlorine* and *bromine* form substitution-products (p. 1065).

4. *Iodide of ethyl* heated with codeine forms hydriodate of ethyl-codeine.

5. Codeine gently heated with *hydrate of potassium*, yields several volatile alkalis, viz. ammonia, methylamine and tritylamine, in variable proportion, according to the manner in which the process is conducted. A volatile crystalline base is likewise produced in small quantity, and a brown or black substance remains.

Salts of Codeine.—Codeine is a mono-acid base, dissolving readily in acids, and yielding for the most part crystallisable salts. They are very bitter, are not reddened by nitric acid, and do not impart a blue colour to ferric salts. *Potash* precipitates codeine from their solutions; *ammonia* does not precipitate them immediately, but gives rise, after some time, to the separation of small transparent crystals of codeine. *Infusion of gall-nuts* precipitates codeine-salts immediately.

Chromate of Codeine is easily obtained in beautiful yellow needles.

Hydrochlorate of Codeine, $C^{18}H^{21}NO^3.HCl + 2H^2O$.—A somewhat concentrated solution of codeine in hydrochloric acid, solidifies completely on cooling; a more dilute solution deposits radiate groups of short needles, exhibiting under the microscope the form of prisms with four faces, terminated by dihedral summits. The crystals dissolve in 20 pts. of water at 15·5°C., and in less than their weight of boiling water. They give off $\frac{1}{2}$ of their water at 100° C., the remainder at 121°, part of the acid, however, going off at the same time.

Chloro-aurate of Codeine, obtained by mixing the solutions of the component salts, is a reddish or light-brown precipitate, moderately soluble in hydrochloric acid.

The *Chloromercurate* is obtained in like manner, as a precipitate, soluble in boiling water and in alcohol, and deposited in stellate groups on cooling.

The *Chloroplatinate*, $C^{18}H^{21}NO^3.HCl.PtCl^2 + 2H^2O$ separates on adding dichloride of platinum to a moderately concentrated solution of hydrochlorate of codeine, as a light-yellow powder, which, if left in the liquid or kept moist on the filter, gradually becomes crystalline, and of an orange-red colour. From very dilute solutions, the double salt separates after some time in silky needles. It dissolves sparingly in cold water, and is decomposed by boiling water. It gives off $\frac{3}{4}$ of its water at 100° C., the rest at 120°, with incipient decomposition.

Hydriodate of Codeine. $C^{18}H^{21}NO^3.HI + H^2O$.—Long thin needles, soluble in about 60 pts. of cold water, much more soluble in boiling water. They do not give off any water at 100° C.

Hydrocyanate of Codeine is uncrystallisable.—The *hydroferrocyanate*, produced by mixing the alcoholic solutions of codeine and hydroferrocyanic acid, is a white precipitate which crystallises after a while in needles, and dissolves in excess of hydroferrocyanic acid. The *hydroferricyanate* produced by adding aqueous ferricyanide of potassium to hydrochlorate of codeine, is a very unstable crystalline compound.

Nitrate of Codeine, $C^{18}H^{21}NO^3.HNO^3$, is produced by slowly adding nitric acid of specific gravity 1·06 to pulverised codeine, carefully avoiding an excess of the acid, which would produce decomposition. It dissolves easily in boiling water, and separates on cooling in small prismatic crystals. It melts at a moderate heat, and decomposes at a higher temperature, leaving a difficultly combustible charcoal.

Oxalate of Codeine, $2C^{18}H^{21}NO^3.H^2C^2O^4 + 3H^2O$, is deposited on cooling, from a hot saturated solution in short prisms and sometimes in scales. It dissolves in 30 pts. water at 15·5° C., and in about half its weight of boiling water. It gives off its water at 100°, turns brown at about 121°, and decomposes completely at higher temperatures.

Phosphate of Codeine. $C^{18}H^{21}NO^3.H^3PO^4 + \frac{3}{2}H^2O$—A solution of ordinary phosphoric acid saturated with pulverised codeine does not crystallise by concentration, but on addition of strong alcohol immediately deposits scales or short prisms. It is very soluble in water.

Other phosphates of codeine appear also to exist.

Sulphate of Codeine, $2C^{18}H^{21}NO^3.H^2SO^4 + 5H^2O$ (or $C^{36}H^{21}NO^6.HSO^4 + 5HO$) crystallises in radiate groups of long needles, or by spontaneous evaporation, in flattened prisms. It dissolves in 30 pts. of cold water, and is very soluble in hot water. When pure, it is neutral to test-paper; but it is apt to retain a small quantity of acid, which may be separated by repeated crystallisation. The crystals belong to the trimetric system, $\infty P . \breve{P}\infty . \infty\bar{P}\infty$. Inclination of $\infty P : \infty P = 151° 12'$; $\infty\bar{P}\infty : \breve{P}\infty = 113° 45'$; $\breve{P}\infty : \breve{P}\infty = 133° 3'$; $\infty\bar{P}\infty : \infty P = 104° 24$. Cleavage parallel to $\infty\bar{P}\infty$.

Sulphocyanate of Codeine. $C^{18}H^{21}NO^3.HCyS + \frac{1}{2}H^2O$.—Radiate needles melting at 100° C., giving off 2·45 per cent. water (= $\frac{1}{2}$ at.) at 100° C.

Tartrate of Codeine is uncrystallisable.

Substitution-products of Codeine.

Bromocodeine. $2C^{18}H^{20}BrNO^3 + 3H^2O$ (Anderson *loc. cit.*)—Prepared by adding bromine-water in small successive portions to pulverised codeine. The codeine dissolves, and the solution loses the colour of bromine but acquires a characteristic reddish tint. On adding ammonia, the whole of the bromocodeine is precipitated as a silver-white powder, containing a small quantity of unaltered codeine. It may be obtained pure by repeated washing with cold water, solution in hydrochloric acid, precipitation with ammonia and crystallisation from alcohol.

Bromocodeine is nearly insoluble in cold water, rather more soluble in hot water, whence it separates on cooling in small prisms with dihedral summits. It is nearly insoluble also in ether, but dissolves easily in alcohol, especially at the boiling heat. Better crystals are obtained from alcohol diluted with an equal volume of water. The crystals are always very small, but of dazzling whiteness. They give off their water (6·66 per cent.) at 100° C. The anhydrous base gives by analysis 57·44 per cent. C, 5·44 H, and 21·5 Br, the formula $C^{18}H^{21}BrNO^3$, requiring 57·14 C, 5·29 H, 21·16 Br, 3·70 N, and 12·71 O.

Bromocodeine melts when heated, forming a colourless liquid, which decomposes at a somewhat higher temperature. It dissolves in cold sulphuric acid, the solution becoming dark coloured when heated. It is attacked by nitric acid, but much less quickly than codeine.

Hydrobromate of Bromocodeine, $C^{18}H^{20}BrNO^3.HBr + H^2O$, forms small prisms, sparingly soluble in cold water, very soluble in boiling water. It gives off its water at 100° C. The *hydrochlorate* forms radiate needles, resembling hydrochlorate of codeine. The *chloroplatinate*, $C^{18}H^{20}BrNO^3.HCl.PtCl^2$ (at 100° C.), is precipitated as a pale-yellow powder, insoluble in water and in alcohol (platinum, by analysis, 16·98 per cent.; by calculation 16·89).

Tribromocodeine, $C^{18}H^{18}Br^3NO^3$ (Anderson, *loc. cit.*)—When bromocodeine is subjected to the continued action of bromine-water in excess, a light-yellow precipitate of hydrobromate of tribromocodeine is formed, which redissolves at first, but becomes permanent on further addition of bromine. On leaving the liquid to itself for 24 hours and then adding more bromine, a fresh precipitate is formed, and this treatment must be repeated day after day as long as any further precipitate is thrown down by adding bromine. The yellow precipitate is then to be washed with cold water, and dissolved in hydrochloric acid; and the base precipitated by ammonia, purified by solution in alcohol, and precipitated by water.

Tribromocodeine thus prepared is an amorphous bulky powder, grey when dry, insoluble in water and ether, easily soluble in alcohol. It dissolves somewhat sparingly in cold, more easily in hot hydrochloric acid, a small portion however remaining undissolved, apparently from partial decomposition. It turns brown when heated on platinum-foil, and decomposes completely at its melting point, leaving a very slowly combustible charcoal.

Tribromocodeine is but a weak base; its salts are all soluble in water and amorphous. The *hydrobromate*, $2C^{18}H^{18}Br^3NO^3.3HBr$, obtained as above, is a light-yellow perfectly amorphous powder, sparingly soluble in cold, more soluble in hot water. The *chloroplatinate*, $C^{18}H^{18}Br^3NO^3.HCl.PtCl^2$, is obtained by precipitation, as a brown-yellow powder, insoluble in water and in alcohol (platinum, by analysis, 13·07 per cent.; by calculation, 13·29).

CHLOROCODEINE, $2C^{18}H^{20}ClNO^3 + 3H^2O$. (Anderson, *loc. cit.*)—Dry codeine treated with chlorine gas, yields a number of complex products, which have not been examined. By passing chlorine into the aqueous solution of codeine, a nearly black liquid is produced, from which ammonia throws down an amorphous resinous base. A more definite reaction is obtained by treating codeine with chlorate of potassium and hydrochloric acid. Finely pulverised chlorate of potassium is gradually added to a solution of codeine in hydrochloric acid at 65°—70° C. till the liquid yields a precipitate on addition of ammonia. Excess of ammonia is then added, which throws down chlorocodeine as a silver-white or generally somewhat yellowish crystalline powder, while a reddish liquid remains, containing products of a further decomposition. In this process, the same precautions must be observed as in the preparation of nitrocodeine (p. 1068). The chlorocodeine is freed from a small quantity of undecomposed codeine by solution in hydrochloric acid, boiling with animal charcoal, precipitation with ammonia, and crystallisation from a hot alcoholic solution.

Chlorocodeine resembles bromocodeine in most of its properties. It dissolves sparingly in boiling water, and crystallises on cooling in small prisms, which appear to be isomorphous with the crystals of bromocodeine. It is very soluble in strong alcohol, especially if hot; sparingly soluble in ether. The crystals give off their water (7·48 per cent.) at 100° C. The dried base gives by analysis 65·31 per cent. C, 6·11 H, and 10·32 Cl, the formula $C^{18}H^{20}ClNO^3$ requiring 64·76 C, 5·99 H, 10·64 Cl, 4·19 N, and 14·42 O.

Chlorocodeine dissolves without alteration in strong sulphuric acid; but the solution is carbonised by heat. Nitric acid also dissolves it, and the solution decomposes on boiling, though, much less easily than that of codeine, giving off nitrous gases and a very pungent vapour.

The *salts of chlorocodeine* resemble those of bromocodeine. The *chloroplatinate* is a pale yellow precipitate, which after drying at 200° C. yields 18·29 per cent

Pt.; agreeing with the formula $C^{18}H^{20}ClNO^3.HCl.PtCl^2$. The *sulphate*, $2C^{18}H^{20}ClNO^3, H^2SO^4 + 8H^2O$ is deposited from a hot solution in radiate groups of short prisms, very soluble in boiling water and in alcohol.

Cyanocodeine, $C^{18}H^{21}NO^3.Cy^2$ (Anderson, *loc. cit.*)—This compound, which is not a substitution-product like the preceding, but rather a cyanide of codeine, is produced when cyanogen gas is slowly passed into a concentrated alcoholic solution. The gas is abundantly absorbed, the liquid first turning yellow, then brown; the odour of cyanogen gradually disappears, and is replaced by that of hydrocyanic acid; and crystals are deposited, continually increasing in quantity, as the passage of the gas is continued. The mother-liquor separated from the crystals yields an additional quantity if again treated with cyanogen gas. The crystals are washed with a small quantity of alcohol, and dissolved in a hot mixture of ether and alcohol, into which solution cyanogen is again passed to transform any codeine that may have remained unacted on. Cyanocodeine then separates in thin, shining, colourless or faintly yellow, six-sided laminæ. It dissolves easily in boiling absolute alcohol, or in a mixture of alcohol and ether, sparingly in water, more easily on addition of alcohol; this solution however does not deposit anything when left at rest, and decomposes by evaporation, leaving a residue of codeine.

Cyanocodeine yields by analysis 68·13 per cent. C, 6·05 H, and 11·66 N, calculation requiring 68·37 per cent. C, 5·97 H, 11·68 N, and 13·97 O.

[It is perhaps a hydrocyanate of cyanocodeine, $C^{18}H^{20}CyNO^3.HCy$.]

With *hydrochloric acid*, it forms a crystallisable salt, which however quickly decomposes, giving off ammonia on addition of potash; the hydrochloric acid solution, if left to stand for twenty-four hours, gives off hydrocyanic acid. With *oxalic* and *sulphuric* acids, cyanocodeine forms sparingly soluble salts which likewise decompose quickly, giving off ammonia and hydrocyanic acid. (Anderson.)

Ethylcodeine, $C^{20}H^{25}NO^3 = C^{18}H^{20}(C^2H^5)NO^3$. (H. How, Chem. Soc. Qu. J. vi. 125.)—The hydriodate of this base is obtained by enclosing in a sealed tube pulverised codeine with a small quantity of iodide of ethyl and sufficient absolute alcohol to dissolve the codeine, and heating the mixture in the water-bath for two hours. On cooling, a crystalline mass is obtained, very soluble in cold water, whence it is deposited, after concentration, in tufts of fine needles. Dried at 100° C., it contains 52·59 per cent. C, 5·87 H, and 27·91 I, agreeing nearly with the formula $C^{20}H^{25}NO^3,HI$, which requires 52·73 C, 5·76 H, and 27·92 I.

The solution is not precipitated either by potash or by ammonia. Treated with oxide of silver, it yields a strongly alkaline liquid which absorbs carbonic acid during evaporation. The residue is again attacked by iodide of ethyl, but the reaction appears to be very complicated.

Iodocodeine, $C^{18}H^{21}NO^3.I^3$. (Anderson, *loc. cit.*)—This compound—which should rather be called iodide of codeine, for it is not a substitution-product—is prepared by dissolving equal weights of iodine and codeine in the smallest possible quantities of alcohol, mixing the solutions, and leaving the mixture at rest; iodocodeine is then deposited, after a longer or shorter time, according to the concentration of the solutions, in triangular plates belonging to the triclinic system; they have a fine ruby colour by transmitted light, deep violet by reflected light, and if well illuminated, exhibit a beautiful adamantine, nearly metallic lustre. They are insoluble in water and in ether, but dissolve in alcohol with red-brown colour. After drying in vacuo, they contain, according to the mean of Anderson's analyses, 32·07 per cent. C, 3·39 H, and 55·32 I, the formula requiring 31·75 C, 3·08 H, and 56 I.

Iodocodeine gives off iodine at 100° C. It is dissolved by hot sulphuric acid, and slowly attacked by hot nitric acid. Boiling potash dissolves out the iodine and leaves codeine. With sulphuretted hydrogen, it yields hydriodate of codeine, with deposition of sulphur. With nitrate of silver, it forms an immediate precipitate, which, however, contains only about $\frac{7}{8}$ of the iodine in the compound. (Anderson, *loc. cit.*)

Nitrocodeine, $C^{18}H^{20}N^2O^5 = C^{18}H^{20}(NO^2)NO^3$. (Anderson, *loc. cit.*)—To prepare this base, dilute nitric acid, of specific gravity 1·060, is heated in a flask to a temperature short of ebullition, finely pulverised codeine is added, and the mixture is kept at a gentle heat for a few minutes, till a sample of it gives a precipitate with ammonia, and the quantity of this precipitate no longer increases after several trials. The whole of the solution is then saturated with ammonia and briskly agitated, whereby a thick precipitate of nitrocodeine is formed. The action of the nitric acid is very rapid, the transformation being complete in a few minutes, so that close watching is necessary to seize the exact point at which the liquid should be saturated with ammonia. Evolution of red vapours is a sign that the action has gone too far, and that a portion of the codeine has been converted into a peculiar red substance, not yet examined. In this case, it is best to interrupt the process before the whole of the codeine is decomposed. Strong nitric acid acts on codeine with violence, producing a yellow resin.

Nitrocodeine precipitated by ammonia, as above, forms very small silvery laminæ, slightly tinged with yellow. It is purified from colouring matter and a little unaltered codeine, by solution in hydrochloric acid, boiling with animal charcoal, reprecipitation by ammonia, and recrystallisation from dilute alcohol or ether-alcohol. From alcohol it crystallises in thin silky laminæ of a pale tawny colour, forming, when dry, an interlaced silky mass. From ether-alcohol it separates, by evaporation, in small yellowish crystals, exhibiting under the microscope the form of quadrilateral prisms with dihedral summits. It is sparingly soluble in boiling water, and separates in small crystals on cooling. It dissolves readily in boiling alcohol, sparingly in ether. It gives by analysis 62·49—63·10 C, and 5·91—6·04 H, the formula requiring 62·79 C, and 5·81 H.

Nitrocodeine when cautiously heated melts to a yellow liquid, which solidifies to a highly crystalline mass. At a higher temperature, it decomposes quickly, without flame, leaving a bulky charcoal. When the alcoholic solution of nitrocodeine is treated with sulphide of ammonium at the heat of the water-bath, it acquires a dark colour and deposits sulphur. When the action is complete, the filtered liquid yields with ammonia a brown amorphous precipitate, which, after solution in hydrochloric acid, boiling with animal charcoal, and reprecipitation, forms a pale yellow basic substance (*azocodeine*), which has not been further examined.

Nitrocodeine dissolves in acids, forming salts which are neutral to test-papers, and from which the base is precipitated as a crystalline powder by potash or ammonia.

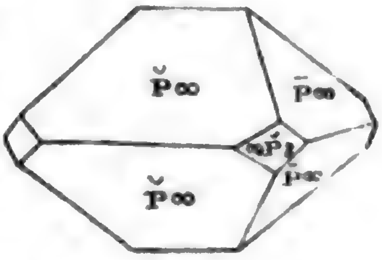
The *hydrochlorate* is obtained by evaporation in the form of an uncrystallisable resinous mass. The *chloroplatinate*, $C^{18}H^{20}(NO^2)NO^3.HCl.PtCl^2 + 2aq.$, is a yellow precipitate, insoluble in water and in alcohol. It gives off its water at 100° C., and then yields by analysis 17·88 per cent. Pt (calc. 17·93).

The *oxalate* crystallises in short yellow prisms, very soluble in water. The *sulphate*, $2C^{18}H^{20}(NO^2)NO^3.H^2SO^4 + 2aq.$ (at 100° C.), is obtained in radiate groups of short pointed needles, neutral to test-paper, and very soluble in boiling water.

COD-LIVER OIL. See OILS, ANIMAL.

CŒLESTIN. Sr^2SO^4 or $SrO.SO^3$.—Native sulphate of strontium. This mineral is so named from its occasional delicate blue colour; though it is frequently found of other shades, as white, greyish and yellowish-white, and red. It occurs massive, and crystallised, sometimes also in fibrous and stellated forms. It belongs to the trimetric system, being isomorphous with sulphate of barium and sulphate of calcium. The primary form is a rhombic prism of 104° 20′ and 75° 40′. An ordinary combination is $\bar{P}\infty$. $\breve{P}\infty$. $\infty\breve{P}2$ (*fig.* 128). Cleavage very distinct parallel to $\breve{P}\infty$; less distinct parallel to $\bar{P}\infty$. It has a vitreous lustre, and is transparent, translucent, or opaque. It is very brittle. Specific gravity 3·953 (Breithaupt). Hardness 3—3·5. Before the blowpipe it fuses to a white, opaque, friable enamel. Cœlestin occurs abundantly in the massive form at Montmartre, and near Bristol. The crystallised variety is found in the red sandstone at Inverness, and in many other localities. Splendid groups of crystals occur at Girgenti in Sicily, mixed with sulphur and gypsum. Fine specimens are also met with at Bex in Switzerland, Conil in Spain, Retzbanya in Hungary, in compact limestone near Lake Erie, and many other localities. Crystals of cœlestin are often found in which the strontium is partially replaced by barium or calcium, the substitution being attended with a certain alteration in the magnitude of the angles of the crystal. The blue colouring of certain specimens of cœlestin appears to be due to the presence of small quantities of ferroso-ferric phosphate. (Jahresber. f. Chem. 1847, 1219; 1849, 776; 1850, 757; 1853, 842; 1855, 970; 1856, 874; 1857, 692.—Dana, ii. 368.)

Fig. 128.



CŒLOCLINE POLYCARPA. The tree which yields the Abeocouta bark of West Africa, where it is used for colouring skins, mats, &c.; also as a local application for ulcers. According to Stenhouse, the bark contains berberine.

CŒRULIC ACID. According to Vlaanderen and Mulder (Jahresb. d. Chem. 1858, p. 262), caffeic or caffetannic acid (i. 709), which they regard as $C^{14}H^{16}O^7$, yields by oxidation, *caffeanic* acid, $C^{14}H^{16}O^8$, and from this, by the action of air and ammonia, are produced *α-cærulic* acid, $C^{14}H^{16}O^9$, and *β-cærulic* acid, $C^{14}H^{14}O^8$, both of which form blue salts, and consequently resemble viridic acid (*q. v.*)

CŒRULIN. A name sometimes applied to the body $C^8H^{15}NO$, supposed to exist in sulphindigotic acid, $C^8H^{15}NO.SO^3$.

COFFEE. *Café. Kaffee.*—Coffee beans are the seed of *Caffea arabica*, a tree of the rubiaceous order, indigenous in southern Abyssinia. It is said to have been transplanted into Arabia at the beginning of the fifteenth century, and the cultivation has since been extended to the West Indies, Brazil, Java, Ceylon, and other warm countries. The seeds are separated from the soft pods by bruising with a heavy roller, then washed and dried, and lastly freed from their parchment-like coating by passing them under a wooden edge-wheel, and subsequently winnowing. In this state they are sent to Europe.

The most highly esteemed variety is the Mocha coffee, which is grown in the province of Yemen in Arabia: it has a more agreeable taste and smell than any other kind, and is distinguished by its yellow colour and the comparative smallness and roundness of the bean. Next to it in European reputation, are the Martinique and Bourbon coffees; the former is larger than the Arabian and more oblong; it is rounded at the ends, of greenish colour, and almost always retains a silver-grey pellicle which comes off in roasting. The Bourbon coffee approaches nearest to the Mocha, from which it originally sprung. The Saint Domingo coffee, which has its two extremities pointed, is much less esteemed than the preceding.

The chemical properties and composition of coffee beans have been made the subject of numerous investigations. Schroeder in 1808 (Gehler's J. Chem. Phys. vi. 564), showed that they contain fat, resin, mucus, extractive matter, &c., and that the aqueous extract is coloured green by ferroso-ferric salts, and yields a green precipitate with copper-salts on addition of an alkali.—Runge in 1820 (*Materalien zur Physiologie*, Lief i. p. 146) discovered caffeine: and Pfaff (*Syst. d. Materia Medica*, iii. 3) found in the beans, in addition to this substance, two acids, viz. caffeic and caffetannic acids, which, however, were afterwards shown by Rochleder to be identical. The examination of coffee-beans was further carried out by Robiquet and Boutron (J. Pharm. xxiii. 101), who found, in addition to fat, extractive matter, and caffeine, a white crystallisable substance, and an acid precipitable by neutral acetate of lead;—by Rochleder (Ann. Ch. Pharm. l. 224; lix, 300; lxiii. 193; lxvi. 35), who found legumin, and a very small quantity of citric acid (a few grains in a pound of coffee);—afterwards by Payen (Ann. Ch. Phys. [3] xxvi. 108), von Bibra (*Narkotische Genussmittel*, u. s. w. Nürnberg, 1855), and lastly by Graham, Stenhouse, and Campbell (Chem. Soc. Qu. J. ix. 33). According to Payen, the caffeine exists partly in the free state, partly as caffetannate of caffeine and potassium (a view considered as doubtful by Graham, Stenhouse, and Campbell). Payen also found sugar in the unroasted beans. According to Graham, Stenhouse, and Campbell, the unroasted beans contain, partly cane-sugar, partly another kind of sugar, probably in combination as a glucoside, the total amount of sugar in various kinds of coffee varying from 6·0 to 7·5 per cent. The caffeine amounts to 1·0 per cent. according to Payen; from 0·5 to 1·0 according to Graham, Stenhouse, and Campbell. The amount of fat appears to vary considerably. According to Rochleder, the beans contain olein and palmitin, perhaps also laurostearin. Robiquet and Boutron found in 8 pts. of Martinique coffee, 1 pt. of fat. Payen found that Mocha coffee contains about 13 per cent. of fat, which is rather greater than the proportion in Martinique coffee. The fat of Mocha coffee also retains the odoriferous principle more tenaciously than that of other varieties; it is yellowish, very fluid, and separates only into two portions of different melting points, whereas that of Martinique coffee has a more brownish colour, is less fluid, and may be separated into at least four distinct fats, melting at about 5°, 20°, 50°, and 90° C. respectively, the last being a kind of vegetable wax. According to Stenhouse, coffee beans contain about 12 per cent. of fat. According to Vogel, benzene extracts from them 18 per cent. of soluble matter.

The following is the average composition of raw coffee beans, as determined by Payen and von Bibra:—

	Payen.		v. Bibra.
Cellulose	34	Woody fibre	36 to 59
Water	12	Water	5 to 9
Fat	10 to 13	Fats	3 to 5
Glucose, dextrin, and organic acid	15·5	Sugar	6 to 7
Legumin and Casein	10	Vegetable casein	undetermined
Other nitrogenous substances	3		
Caffeine (free)	0·8	Caffeine	0·2 to 0·8
Caffetannate of caffeine and potassium	3·5 to 5·0	Essential oil	not weighable
Viscid essential oil (insoluble in water)	0·001	Substances precipitable by neutral acetate of lead	7 to 8
Aromatic oils, some lighter, others heavier than water	0·002	Precipitable by basic acetate of lead	5 to 6
Ash	6·7	Ash	6 to 7

Levi (Ann. Ch. Pharm. l. 421) found 3·2 per cent. ash.—**T. J. Herapath** (Chem. Gaz. 1848, p. 159) found 6·7 per cent. in the dry beans. Vogel found 3·5 per cent. ash, of which 0·80 was soluble in water.

Composition of the Ash of Coffee-beans in 100 *parts.*

			Graham, Stenhouse, and Campbell.						
	Levi.	Herapath.	Ceylon cult.	Ceylon wild.	Java.	Costa Rica.	Jamaica.	Mocha.	Neil-gherry.
Potash . . .	50·9	16·5	55·1	52·7	54·0	53·2	53·7	51·6	55·8
Soda	14·8	7·1							
Lime	4·8	27·7	4·1	4·6	4·1	4·6	6·1	5·9	6·7
Magnesia . .	10·9	5·9	8·2	8·5	8·2	8·7	8·4	8·9	8·5
Ferric oxide .	0·6		0·45	0·98	0·73	0·63	0·44	0·44	0·61
Sulphuric acid anhydrous .	trace.	1·3	3·6	4·5	3·5	3·8	3·1	5·2	3·1
Carbonic acid anhydrous .	—	—	17·5	16·9	18·1	16·9	16·4	17·0	14·9
Phosphoric acid anhydrous	13·6	40·7	10·3	11·6	11·0	10·8	11·1	10·1	10·8
Chlorine . . .	1·2	0·4	1·1	0·5	0·8	1·0	0·7	0·6	0·6
Silica	3·6	0·4							

From the analysis of the six varieties by Graham, Stenhouse, and Campbell, which exhibit a remarkably close agreement, it appears that coffee-ash is especially distinguished by the absence of soda and silica. The soda found by Levi is doubtful, and Herapath's results, which differ enormously from all the rest, may be rejected as untrustworthy.

Roasting Coffee.—Coffee-beans, when heated or roasted, assume a light brown, chestnut-brown, or even black colour, according to the degree of heat applied. The air-dried beans diminish in weight during roasting by 15 or 25 per cent., but increase considerably in volume, the increase amounting, according to v. Bibra, to from 50 to 58 per cent., if they have been previously washed, or if they are strongly heated. According to Payen, 100 grms. of raw coffee-beans yield 50 grms. of roasted beans, and 100 vols. of the beans increase by roasting to 130 vols. To roast the beans with perfect regularity, it is best to steep them in water for ten or twelve minutes, then to dry them lightly, after draining, and roast them immediately. The steeping removes impurities, and perhaps also serves to impart to the beans a uniform amount of water, so that they get more regularly heated.

The vessels used for roasting coffee are generally of iron: recently silver and glass vessels have also been used for the purpose. The chief point to be attended to in their construction and use, is to ensure that the heat be gradual and not too strong. If the beans are heated above the temperature required to brown them, they swell up strongly, turn black, and ultimately become carbonised. (See *Ure's Dictionary of Arts, Manufactures, and Mines*, i. 794.)

By heating coffee-beans in a retort with proper condensing apparatus, the following volatile products are successively obtained (v. Bibra):

1. A volatile oil, pre-existing in the raw beans, and little, or not at all altered by heat.
2. Volatile oil having the odour of roasted coffee.
3. Empyreumatic oil.
4. A fatty body.
5. Acetic acid.
6. A small quantity of caffeine, together with an aromatic body, probably assamar (i. 428).
7. Humoïd substances, and one or more compounds which easily reduce gold and silver-salts.

The statement of Rochleder that pyrocatechin is formed in the distillation (from the caffetannic acid), is not confirmed by the observations of Graham, Stenhouse, and Campbell.

The composition of roasted coffee has been investigated by Payen, by v. Bibra, and by Graham, Stenhouse, and Campbell. Payen exhausted 100 grms. of ground coffee with a litre of boiling water; heated the filtrate in a distillatory apparatus for two hours, by which time it had quite lost its odour; and collected the distillate in four connected receivers, the first of which gradually became heated to about 90° C., while the second was kept between 25° and 30°, and the third and fourth were cooled to 0°, or a little below, the vapours which escaped from the fourth being passed through strong sulphuric acid, or through a tube filled with red-hot oxide of copper.

In the first receiver, a yellowish water collected, and a few drops of oil, amounting to about $\frac{1}{10}$ of the infusion, floated on the surface, quite destitute of fragrance. The liquid condensed in the second receiver amounted to about $\frac{1}{100}$ of the volume of the infusion: a few drops of an odourless fixed oil floated on the top of the watery liquid, which possessed the fragrant odour of coffee in so high a degree that a few drops of it sufficed to impart the odour to a cup of milk. The water of this second receiver contained the principal part of the coffee-aroma, concentrated about 100 times. On agitating the water with about $\frac{1}{3}$ of its volume of ether, repeating this treatment several times, and then evaporating the ether, there remained a yellowish oil (about 0·1 grm. from 10 grms.), the very strong odour of which resembled that of the aroma common to the several varieties of coffee. Another oil, somewhat more volatile, and of more delicate aromatic odour, remained, together with a little ether, in the water: this oil appears to be contained especially in the finer kinds of coffee, as that of Mocha.

To obtain the whole of the oils from the infusion of coffee, lumps of chloride of calcium are introduced into the first two receivers during the distillation; the third receiver is connected with a chloride-of-calcium-tube and cooled to + 20° C. A solution of chloride of calcium is then obtained, containing the whole of the volatile coffee-oil, which may be extracted from it by agitation with ether. Payen obtained from 10,000 pts. of coffee only 2 pts. of this oil, but possessing so strong an odour that a single drop sufficed to fill a whole room with the characteristic odour of coffee.

If the third receiver be cooled to − 2° or − 3° C. during the distillation, a few drops of liquid collect in it having the odour of coffee, but likewise the less agreeable odour of empyreumatic hydrocarbons, which are present in greater quantity in proportion as the coffee has been more strongly roasted. The odour of these bodies is perceptible also in the fourth receiver and in the vapours which escape therefrom, these vapours likewise imparting a brown colour to oil of vitriol.

According to Zenneck, the aroma of coffee is obtained in larger quantity by adding sulphuric acid to the liquid in the retort.

Von Bibra, by exhausting roasted coffee-beans with ether, obtained from Mocha coffee 8·8 to 9·3 per cent. fatty matter; from Java coffee 8·9 to 9·2 per cent. He supposes that this fat is for the most part produced during the roasting, inasmuch as the raw beans yielded only from 4 to 5 per cent. of fat; and, if the beans thus exhausted were subsequently roasted, they yielded an additional 4 to 6 per cent. fat on being again treated with ether. It is possible, however, that the fat in the raw bean is enclosed in cells, and does not become accessible to the ether till the envelopes are burst by the heat.

The fat extracted by ether has the consistence of cacao-butter (i. 699), and exhales the peculiar aroma of coffee, which appears to be produced from the volatile oil of the raw beans by roasting; by boiling the fat with water this aroma is driven off. The fat is a mixture of several substances, some of which are likewise soluble in alcohol. It appears to contain olein and palmitin, together with a resin and a hydrocarbon; perhaps also other bodies. The ethereal extract likewise contains the whole of the caffeine, and a body which colours iron-salts greenish, precipitates lead-salts, and reduces gold and silver-salts.

When ground coffee which has been exhausted with ether, is twice heated with boiling water, after drying, a dark brown, strongly acid liquid is obtained, having a very bitter taste, but without the peculiar agreeable flavour of coffee. The aqueous extract likewise contains sugar, humoïd substances, assamar, and tannic acid, nearly identical with caffetannic acid; also a substance which reduces gold- and silver-salts, a small quantity of empyreumatic oil, salts, and indifferent substances insoluble in alcohol. The brown bitter products in roasted coffee appear to be produced chiefly from the sugar, inasmuch as that substance diminishes greatly in quantity, or disappears altogether, in the roasting process. Graham, Stenhouse and Campbell found that, whilst the raw beans contained 5·7 to 7·8 per cent. sugar, the roasted beans never contained more than 1·1 per cent., and in many instances none at all.

The residue, after extraction with ether and water, yielded by boiling with water containing carbonate of sodium, a solution coloured deep brown by humoïd substances.

Decoction of coffee does not contain albumin or legumin.

Graham, Stenhouse, and Campbell found in roasted coffee, a brown volatile oil (the *caffeone* of Boutron and Frémy), heavier than water, easily soluble in ether, sparingly in boiling water, but communicating to the water a strong aromatic odour. They also found from 2·5 to 3·0 per cent. nitrogen and sometimes a little sugar.

Von Bibra finds that when ground coffee is treated with boiling water in a French coffee-machine,—in which the boiling water is forced by the pressure of its own vapour from the lower vessel into the upper, which contains the coffee,—from 10 to 12 pts. out of 100 of the coffee pass into the solution: by complete exhaustion, a larger proportion would of course be dissolved. The proportion of soluble matter is increased, up to a certain point, by strong roasting. According to Cadet, coffee roasted to a red-brown colour yields 12·3 per cent.; chestnut-brown coffee 18·5 per cent.; and dark brown 23·7 per cent. of soluble constituents. Payen obtained 37 per cent., and the residue, after thorough exhaustion with water, yielded only 1·2 per cent. ash, ⅓ of which consisted of soluble salts. Lehmann found in roasted Java coffee, 21·5 per cent. soluble matter. Vogel found 39 per cent. (in the raw beans only 25 per cent.). Soft water dissolves out more than hard water; water containing carbonate of soda most of all.

The aqueous extract of coffee yields 16·6 per cent. ash, containing 51·5 per cent. K^2O, 3·6 Ca^2O, 8·6 Mg^2O, 0·2 Fe^4O^3, 10·0 P^2O^5, 40·0 SO^3, 20·5 CO^2, 2·0 KCl, 0·7 SiO^2, with 0·5 sand and charcoal.

Physiological action.—Coffee acts physiologically in two ways: first, by stimulating the action of the nervous and vascular systems, thereby producing a feeling of cheerfulness and mental activity; secondly, by retarding the transformation of tissue, and thus, to a certain extent, supplying the place of other nutriment. Experience has in fact shown that labourers who habitually take coffee as a beverage, require less nitrogenous food to keep up their strength than those who do not take coffee. The stimulating and invigorating action of coffee appears to depend both upon the empyreumatic oil and the caffeine; the retardation of tissue-transformation, chiefly on the empyreumatic oil, the caffeine acting in this manner only when it is present in considerable quantity. The unpleasant symptoms which sometimes attend an excessive use of coffee, such as headache, trembling, and a peculiar delirious sensation, are mainly due to the caffeine (J. Lehmann, Ann. Ch. Pharm. lxxxvii. 207). The assamar and tannic acid in roasted coffee doubtless also contribute in some way to its physiological action.

Tea resembles coffee in containing theine (identical with caffeine) and tannic acid; and, accordingly, its action resembles that of coffee to a certain extent; it differs from coffee, however in not containing the peculiar empyreumatic oils just mentioned, and in being richer in theine and tannin.

Adulteration of Coffee. (Graham, Stenhouse, and Campbell, *loc. cit.*)—Various substances, more or less resembling coffee, are used, either as substitutes for, or additions to it. A great variety of seeds were tried in France during the continuance of the continental blockade, including—in addition to maize, barley, oats, and the other cereals—the seeds of the yellow flag (*Iris pseudo-acorus*), the grey or chick pea (*Cicer arietinum*), the milk vetch or Andalusian astragalus (*Astragalus boeticus*), the *Hibiscus esculentus*, the holly, Spanish broom, acorns, chestnuts, the small lupine (*Lupinus augustifolia*), peas, haricots, horse-beans, sunflower, pips of the gooseberry and grape eglantine (*Rosa villosa*), and the capsules of box (*Buxus sempervirens*). Of these the yellow flag, a common marsh-plant in England, appears to offer the greatest similarity to coffee; but it is doubtful whether the resemblance extends beyond the aroma of the seed when roasted. Indeed no seed appears to be known which, when roasted and pulverised, forms a true and efficient substitute for coffee, either in the physiological properties or in the chemical composition of the soluble extract. The poorer sorts of coffee-beans are sometimes tinted by dusting them with coloured powders, such as Prussian blue, powder of lime-tree charcoal, green earth, &c., mixed with a little graphite, to give them the silvery appearance of the finer sorts.

The use of certain roots roasted and pulverised, to mix with ground coffee, is, however, much more common. The roots most used for this purpose are those of chicory (*Cichorium intybus*), carrot, beet, rush-nut (*Cyperus esculentus*), earth-nut (*Arachis hypogæa*), scratch-weed (*Galium aparine*), fern (*Polypodium filix mas*), and butcher's-broom (*Ruscus aculeatus*).

These roots are prepared by cutting them into thin slices, drying them on a stove, and then passing them through a coffee-roaster, generally with addition of about 2 per cent. of butter, and sometimes of a red powder, to give them the colour of coffee. In this country and in France, the root most used as an addition to coffee is chicory, the annual consumption of which in France amounts to 6,000,000 kilogrammes. In Germany, beet and carrot are extensively used for the same purpose. Not one of these roots contains either caffeine or the peculiar aromatic oils of roasted coffee, and hence they can never serve as efficient substitutes for coffee; but they are valued as an addition to it, because they contain a large quantity of sugar—chicory as much as 30 per cent.—and consequently, when roasted, acquire the peculiar bitter taste and somewhat of the aroma of caramel or burnt sugar, which is well known to be one of the strongest and most general of our gustatory preferences, being that which gives the peculiar flavour to the several varieties of brown beer or porter (i. 529).

The examination of a sample of ground coffee for the detection and estimation of these admixtures, is a matter of some difficulty. As none of the roots contain caffeine, the quantitative determination of that base in the sample may give an approximation to its degree of purity. For this purpose, the coffee may be exhausted by repeated boiling with hot water; the solution concentrated a little by evaporation; the caffetannic acid, and certain other substances, precipitated first by neutral and then by basic acetate of lead; the excess of lead removed from the filtrate by sulphuretted hydrogen; the liquid then evaporated to dryness; the dry matter exhausted with spirit of specific gravity 0·840; and the alcoholic solution concentrated to a nearly syrupy state, and left to stand for ten days. The crystals of caffeine, which then separate, are collected on a small filter, compressed powerfully to remove the mother-liquor, then redissolved in a small quantity of water, and the solution is evaporated and crystallised anew. It yields almost pure caffeine, the quantity of which in the sample is thus determined. Samples of pure coffee of several varieties yielded, by this treatment, from 0·80 to 1·01 per cent. caffeine; if then the amount obtained from a given sample be less than 0·80, the admixture of some other substance may be inferred. (Graham, Stenhouse, and Campbell.)

If it be desired merely to determine whether a given sample of ground vegetable substance contains coffee or not, the search for caffeine may be made by a simpler process, namely, by evaporating the aqueous infusion to dryness after addition of lime, treating the dry mass with ether, leaving the solution to crystallise by evaporation, and testing the crystals with nitric acid and ammonia, whereby, if caffeine be present, the purple colour of murexid is produced (i. 708).

The formation of quinone by the oxidation of caffetannic acid (i. 709), may also be used as a means of recognising the presence of coffee in a mixture. For this purpose the infusion of the powder is evaporated to syrup, and 1 pt. of the residue is distilled with 4 pts. peroxide of manganese, and 1 pt. oil of vitriol diluted with 1 vol. water; quinone is then given off, part subliming in crystals, while the rest passes over with the watery distillate. (Graham, Stenhouse, and Campbell.)

The adulterations of coffee are most easily detected by their physical characters, by the proportion of sugar contained in the sample, and by the composition of the ash.

1. *Action of Water.*—When hot water is applied to the powder of chicory and other roots, it softens immediately, from the facility with which the water is imbibed; whereas the grains of coffee remain hard and gritty. Roasted grain, such as wheat and barley, gives with hot water a thick mucilaginous infusion, while the infusion of coffee is remarkably thin and limpid. The grain-infusion generally contains starch, and gives a blue coloration with iodine, whereas the infusions of both coffee and chicory appear to be quite destitute of starch.

2. *Colouring Power.*—Chicory and the allied roots impart to water a much deeper colour than coffee, the coloration being also much more rapidly produced. By infusing equal quantities of the several substances with boiling water, and observing the colour of the filtered infusions in glass tubes of equal diameter, it was found:—if the colouring power of caramel be represented by 1000, that of chicory is 450, of maize 350, of dandelion-root 300·3, of red beet 300·3, of bread-raspings 274·72, of acorns 200, of highly-roasted coffee 173·31, of medium-roasted coffee 143·88, of peas 73·18, and of brown malt 25. Hence it appears that chicory has more than three times the colouring power of highly-roasted coffee; maize double that of coffee; whereas peas and beans have only about half the colouring power of coffee.

In infusions prepared with cold water, chicory exhibits four times the colouring power of coffee. If a few grains of roasted chicory or any other sweet root be dropped into a glass of cold water, without being stirred, a yellowish-brown colour diffuses rapidly through the liquid, whereas pure coffee gives no sensible colour to the water under similar circumstances.

3. *Specific Gravity of the Infusions.*—Coffee is sharply distinguished from the two most important classes of adulterating substances, the roots and cereals, by the comparatively low specific gravity of its infusion. The comparison may be made by dissolving 1 pt. of the substance in 10 pts. of cold water, raising the temperature to the boiling point, keeping it there for about half a minute, and then filtering. The leguminous seeds give infusions of low specific gravity: peas 1007·3, beans 1008·4. The specific gravity of coffee infusions varies from 1008·0, for Mocha, to 1009·5, that of Costa Rica coffee; that of chicory infusion is much higher, ranging in different samples from 1019·1 to 1023·2. Infusions of cereals stand equally high, or higher, in the scale of gravity, rye-meal giving 1021·6, and maize 1021·5.

4. *Action of Ether.*—The following substances, agitated with ten times their weight of ether, give different proportions of matter soluble in that liquid, viz.:

Roasted beans	1·81	per cent. of oil and resin,
,, maize	5·15	,, ,, ,,
,, chicory (Yorkshire) . .	6·83	,, ,, ,,
,, coffee (Mocha) . .	15·93	,, ,, ,,

the last including probably 1 per cent. of caffeine. Hence it appears that coffee yields to ether much more soluble matter than beans, maize, or chicory, which represent the three classes of leguminous seeds, cereals, and sweet roots. The fat obtained from chicory was doubtless that which is added in the roasting process, to prevent burning. The experiment with ether is easily made, and may sometimes prove valuable.

5. *Quantity of fermentable Sugar.*—The quantity of fermentable sugar in sweet roots, both before and after torrefaction, is much greater than in coffee. By subjecting the different substances to fermentation with yeast, and determining the amount of alcohol in the distillate (see SUGAR), the sugar in raw coffee is found to vary from 6·20 to 7·52 per cent.; that of roasted coffee from 0·0 to 1·14. The proportion in chicory and other sweet roots is given in the following table:

	Sugar per cent.	
	Raw.	Roasted.
Foreign chicory	23·76	11·98
Guernsey „	30·49	15·96
English „	35·23	17·98
„ „ (Yorkshire)	32·06	9·86
Mangold-wurzel	23·68	9·96
Carrots (ordinary)	31·98	11·53
Turnips	30·48	9·65
Beetroot (red)	24·06	17·24
Dandelion root	21·96	9·08
Parsnips	21·70	6·98
Bonka (a coffee substitute)	—	5·82

These numbers are sufficient to show that the fermentation-test affords an easy method of distinguishing these roots from coffee. The leguminous seeds, cereals, and other seeds are not so easily distinguished by this method, the proportion of sugar in the roasted material varying only from 0·74 in lupine seed to 2·70 in acorns.

6. *Composition of the Ash.*—Coffee is remarkably distinguished from the roots and cereals by the small quantity of silica in its ash, which never exceeds 0·5 per cent.; and even this small quantity, which is not always present, probably arises from accidental adhesion of sand to the beans. Chicory-ash, on the other hand, contains (after deducting sand) from 3·81 to 10·52 per cent. silica (i. 962), and roasted dandelion-root 11·26 per cent. The proportion of silica may be determined, without making a formal analysis of the ash, by simply digesting it in strong hydrochloric acid and weighing the residue. In lupines, acorns, maize, and parsnips, the proportion of silica is not large enough to afford a good distinction from coffee; but lupine-ash contains 17·75 per cent. of soda, which, according to Graham, Stenhouse, and Campbell, is not found in coffee-ash; the ashes of lupines and of acorns likewise contain twice as much chlorine as coffee-ash, and in the ash of maize the proportion of phosphoric acid is very high, viz. 44·5 per cent., whereas in coffee-ash it is only about ten per cent. Beetroot ash is distinguished from coffee-ash by its very large amount of chlorine, which varies from about 8 to 29 per cent.

7. *Proportion of Nitrogen.*—The nitrogen in foreign raw chicory amounts to 1·51 per cent. in the roasted root to 1·42 per cent. English chicory gave, in the raw state 1·86, in the roasted state 1·74 per cent. nitrogen. In roasted coffee the proportion of nitrogen is rather greater, viz. about 2·75 per cent.; but the difference is not great enough to afford a good mode of distinction. It may, however, be admitted that less than 2 per cent. of nitrogen in coffee is a strong presumption of adulteration with chicory or some other root.

On the whole, we may conclude that the best indication-tests of the presence of foreign substances in ground coffee are afforded by the colouring power, the specific gravity of the infusion, the fermentation-test, and the composition of the ash.

COFFEE LEAVES. The leaves of the coffee tree have been examined by Stenhouse (Phil. Mag. [4] vii. 21), who received a sample of them, dried at rather too high a temperature, from Sumatra. They were found to contain 1·2 per cent. caffeine, and altogether 2·1 per cent. nitrogen; as some of the caffeine may have been decomposed in the drying of the leaves, the real proportion may perhaps amount to 1·5 per cent. They also appear to contain a larger proportion of caffetannic acid than the beans; the proportion of matter extracted by water was 38·8 per cent. An infusion of the leaves in boiling water has a deep brown colour, and in taste and odour resembles a mixture of tea and coffee. The leaves might therefore, perhaps, be used as a substitute for tea-leaves or coffee-beans. Their use for this purpose was first suggested by Van den Corput in Brussels. (Ann. Ch. Pharm. lxxxix. 244.)

COFFEINE. Syn. with CAFFEINE (i. 707).

COGNAC. The finest kind of French brandy distilled from wine; it takes its name from the town of Cognac, in the Département de la Charente. (See BRANDY, i. 652.)

COHOBATION. The continuous redistillation of the same liquid from the same materials.

COHESION and **ADHESION.** Cohesion is the force by which particles of one and the same body, or homogenous particles in general, are held together. Adhesion that which holds together the particles of two dissimilar bodies when brought into close contact.

These forces appear to act only at distances inappreciable to our senses. When a solid body, as a piece of wood or stone, is broken, the pieces cannot be made to cohere again by merely pressing them together, because the surfaces, being uneven, can only come into contact at a few points, and the cohesive force is imperceptible; but if the bodies touch each other by large flat surfaces, as when two well polished plates of glass or metal are pressed together, they cohere with great force.

The adhesion between the particles of dissimilar bodies is determined by precisely similar conditions. Plates of lead and tin, or of copper and silver, may be almost inseparably united by strong pressure between rollers. Adhesion takes place with peculiar facility when one or both of the bodies is in the liquid state, because the particles, being free to move, can easily adapt themselves to each other. All liquids, like oil and water, which do not mix, adhere with more or less force by their surfaces, and adhesion shows itself in most cases when a liquid comes in contact with a solid body, the liquid being then said to wet the solid. A glass plate suspended from the arm of a balance and made to touch the surface of water requires considerable force to separate it. If the liquid which adheres to the surface of the solid afterwards solidifies, the adhesion becomes still stronger: this is the principle of cementing. When two glass plates are joined together with sealing wax, the adhesion is sometimes so strong that in attempting to part them, particles of the glass separate from each other rather than from the wax.

Notwithstanding the great difference which appears to exist between these molecular forces, and that of gravitation, the former acting only at insensible, while the latter acts at all distances, it is not difficult to show that both kinds of attraction may be merely different modifications of the same power. Let it be assumed that all ultimate atoms attract one another with forces varying directly as their masses and inversely as the squares of the distances between them, and that the aggregates of atoms constituting the physical molecules are not spherical, at least not in all cases. The law of molecular attraction will then depend in great part on the forms and dimensions of these molecules. The attraction between spheres composed of particles which attract one another according to the law of the inverse squares, is the same as if the whole matter of each sphere were concentrated in its centre, that is to say, the spheres attract one another inversely as the square of the distance between their centres. But in bodies of any other shape, the attraction may be regarded as consisting of two parts, one following the law of the inverse squares, just as if the bodies were spherical, the other dependent on the shape of the bodies, and varying inversely as the cube of the distance between their centres of gravity. Such is the case with the attraction of the earth and moon. The equatorial protuberance of the earth produces certain perturbations in the relative movement of the two bodies, which vary in magnitude, according to the law last stated, and would become much more perceptible if the earth and moon were nearer to each other, but would vanish if the distance between them were much greater than it is: for example, if the distance were diminished to $\frac{1}{10}$ of its present amount, the principal part of the attractive force, which determines the elliptical motion, would be increased 100 times, but the disturbing force depending on the figure would be increased 1000 times. If then the law of attraction between the molecules of bodies be affected in like manner by their figures, it will follow that at the extremely small distances existing between the particles of a solid body or of two bodies pressed closely together, the molecular force, which determines the phenomena of cohesion and adhesion, may become almost immeasurably greater than when they are separated by any appreciable distance: for the molecules are so minute that the smallest distance appreciable to our senses may be regarded as infinitely great compared with their dimensions, so that it is only at insensible distances that the influence of their form makes itself felt.

The force of cohesion varies with the temperature and the nature of the body. In gases, in which the dimensions of the actual material particles must be supposed to be infinitely small as compared with the intervals between them, the cohesive force is little, if at all perceptible; in fact, the particles of gases have a constant tendency to fly asunder. (See GASES and HEAT.)

In **liquids**, the distance between the particles is still sufficiently great, compared with their size, to give great freedom of motion, but not sufficient to render the molecular attraction depending on the form of the particles imperceptible; hence liquids, though their particles yield with ease to any external force, nevertheless exhibit, when left to themselves, a tendency to assume the spherical form, that being the arrangement in which a given number of particles occupy the smallest space; since, however, the liquid mass is subject to the influence of other forces, as gravitation and adhesion, the spherical form of a drop is never perfect; this may be seen in the form which drops of mercury assume on glass, or water on glass smeared with fat or lycopodium. As the temperature rises, the cohesive force becomes less, in consequence of the greater separation of the particles; consequently a heated liquid generally forms smaller drops than a cold one. Different liquids exhibit different degrees of cohesion, the cohesive power being very nearly proportional to the density.

In **solids**, the cohesive power shows itself in the highest degree, the particles not being able to move freely over one another, so that an external force, if it does not produce disruption, gives rise to an equal and parallel motion throughout the mass.

The force of cohesion in a solid is measured by the resistance which the body offers to any mechanical force tending to separate the particles. The resistance offered to a force tending to pull the particles asunder is called the **absolute cohesion** or **tenacity**; the lateral resistance to fracture is the **relative tenacity**; and the resistance which the body opposes to a crushing force is sometimes called the **retroactive tenacity** (*rückwirkende Festigkeit*). These three modifications of the cohesive strength have all been made the subject of direct experiment in numerous bodies; they are connected with each other by relations which are capable of exact mathematical analysis, but the investigation of which is foreign to the character of this work.

Absolute tenacity—Muschenbroeck made numerous experiments on the absolute tenacity of bodies; his results are given in the following table, which shows the weights required to break rods or wires of various materials when suspended from them:—

Absolute Tenacities of Solids

	Horizontal section = ¼ square line.	Horizontal section = ¼ sq. centimetre.
Elm-wood	87 pounds	918 kilogr.
Pine (*Pinus silvestris*)	97 „	1021 „
Fir (*Pinus abies*)	57—88 „	600—929 „
Oak	110—140 „	1150—1466 „
Beech	136—148 „	1349—1586 „
Ebony	89 „	934 „
Copper wire	266 „	2782 „
Brass	340 „	3550 „
Gold	442 „	4645 „
Lead	26 „	272 „
Tin	43 „	457 „
Silver	326 „	3411 „
Iron	398 „	4182 „
Glass (white)	14—22 „	142—233 „
Hempen cord	34—60 „	350—360 „

The great variation in the strength of hempen cord arises from the unequal quality of the fibre. Thin cords are comparatively stronger than thick ones, because they are made of better hemp.

The number for gold in the above table is doubtless too high. According to Count Sickingen, the tenacities of different metals are to one another in the following proportions:—

Gold	150955	Copper	304696
Silver	190771	Soft iron (Swedish)	362927
Platinum	262361	Hard iron	559880

The following table exhibits the absolute tenacities of different metals at the temperatures of 0°, 100°, and 200° C., as determined by Baudrimont (Ann. Ch. Phys. [3] xxx. 304.) The upper number opposite each metal gives the highest tenacity observed; the lower number the mean of each set of experiments:

Metals.	Tenacity in grammes for a transverse section of 1 mm. at		
	0°	100°	200°
Gold	19051	15766	13094
	18400	15224	12878
Platinum	23026	20421	18118
	22625	19284	17277
Copper	25338	22050	19839
	25100	21873	18215
Silver	28620	24526	18705
	28324	23266	18577
Palladium	36983	32871	29212
	36481	32484	27077
Iron	209813	201039	213305
	205405	191725	210270

These numbers show that the tenacity diminishes for the most part as the temperature rises; iron, however, exhibits an exception, being more tenacious at 200° than at 100° C.

Resistance to crushing.—The following table is the result of experiments by George Rennie, jun., published in the first part of the *Philosophical Transactions* for 1818.

Mr. Rennie found a cubic inch of the following bodies crushed by the following weights:—

	Crushing weight in lbs. av.
Elm	1284
American pine	1606
White deal	1928
English oak	3860
A prism of Portland stone, 2 inches long	805
Ditto statuary marble	3216
Craigleith stone	8688

Cubes of 1½ inch.

	Sp. gr.	
Chalk	—	1127
Brick of a pale red colour	2·085	1265
Roe-stone, Gloucestershire	—	1449
Red brick, mean of two trials	2·168	1817
Yellow-face baked Hammersmith paviors, three times	—	2254
Burnt ditto, mean of two trials	—	3243
Stourbridge, or fire brick	—	3864
Derby grit, a red friable sandstone	2·316	7070
Derby grit from another quarry	2·428	9776
Killala white freestone, not stratified	2·423	10264
Portland	2·428	10284
Craighleith white freestone	2·452	12346
Yorkshire paving, with the strata	2·507	12856
Ditto, against the strata	2·507	12856
White statuary marble, not veined	1·760	23632
Bramley-Fall sandstone, near Leeds, with strata	2·506	13632
Ditto, against strata	2·506	13632
Cornish granite	2·662	14302
Dundee sandstone, or breccia, two kinds	2·650	14918
A two inch cube of Portland	2·423	14918
Craighleith, with strata	2·452	15560
Devonshire red marble, variegated	—	16712
Compact limestone	2·584	17354
Peterhead granite, hard close-grained	—	18636
Black compact limestone, Limerick	2·598	19924
Purbeck	2·599	20610
Black Brabant marble	2·697	20742

Cubes of 1½ inch (continued).

	Sp. gr.	Crushing weight in lbs. av.
Very hard freestone	2·528	21254
White Italian veined marble	2·725	21783
Aberdeen granite, blue kind	2·625	24556

Cubes of different metals of ¼ inch were crushed by the following weights: —

	lbs. av.
Cast iron	9773
Cast copper	7318
Fine yellow brass	10304
Wrought-copper	6440
Cast tin	966
Cast lead	483

Bars of different metals, 6 inches long, and ¼ of an inch square, were suspended by nippers, and broken by the following weights: —

	lbs. av.
Cast iron, horizontal	1166
Ditto, vertical	1218
Cast steel, previously tilted	8391
Blistered steel, reduced by the hammer	8322
Shear steel, ditto	7977
Swedish iron, ditto	4504
English iron, ditto	3492
Hard gun-metal, mean of two trials	2273
Wrought copper, reduced by hammer	2112
Cast copper	1192
Fine yellow brass	1123
Cast tin	296
Cast lead	114

On the tenacity and other mechanical properties of *cast iron*, a large number of experiments were made by Stephenson, Fairbairn, and Hodgkinson, in connection with the construction of tubular bridges (*The Britannia and Conway Tubular Bridges*, by Clarke, London, 1850; Ann. Min. [4] xx. 427). The experiments on the resistance to direct tension, gave for the absolute tenacity of cast-iron a mean value of 10 to 11 kilogrammes for a square millimetre. The retroactive tenacity was found to be on the average 5·7 times greater than the absolute tenacity.

The tenacity of *glass* has been examined by Fairbairn and Tate (Proc. Roy. Soc. x. 6). The absolute tenacity determined by direct stretching was found to be for:

	Tenacity per sq. in. in lbs.
Flint glass (best; specific gravity 3·0782)	2413
Green glass (specific gravity 2·5284)	2896
Crown glass (extra white; specific gravity 2·4504)	2346

But from experiments on the resistance of glass globes to internal pressures, much higher values were found for the absolute tenacities, viz. for:

	Tenacity in lbs.
Flint glass	4200
Green glass	4800
Crown glass	6000

These results are regarded by the-authorsas more trustworthy than the former, because the globes were better annealed than the rods used in the first experiments.

Experiments on the resistance of glass to crushing were made upon small cylinders and cubes crushed between parallel steel surfaces by means of a lever. The cylinders were cut from rods drawn to the required diameter while hot, and then annealed. The cubes were cut from much larger portions, and were probably less thoroughly annealed. For this reason, the experiments on cylinders, which gave nearly twice the resistance afforded by the cubes, are regarded as the more trustworthy. The following table gives the mean results:

Resistance of Glass to Crushing.

	Mean crushing weight in lbs. per sq. inch.	
	For cylinders.	For cubes.
Flint glass	27582	13130
Green glass	31876	20206
Crown glass	31003	21762

COLCHICEINE, $C^{38}H^{47}N^{2}O^{11}$ (Oberlin, Ann. Ch. Phys. [3] l. 108).—An alkaloïd prepared from colchicine by acidulating the aqueous solution of that body with sulphuric or hydrochloric acid, concentrating the liquid to dryness over the water-bath, then adding water, and crystallising from alcohol the yellow mass which separates. At the same time there is produced, by the action of the acid on the colchicine (perhaps impure), a resin which dissolves in alcohol and in ether, and with deep red colour in ammonia or nitric acid. According to Oberlin, colchiceine exists ready formed in the seeds of *Colchicum autumnale.*

Colchiceine crystallises in colourless nacreous laminæ or needles, sparingly soluble in cold, more easily in boiling water, easily soluble in alcohol, wood-spirit, and chloroform. It melts at 155° C. and becomes coloured at 200°. It dissolves with deep-yellow colour in strong nitric acid; without colour in sulphuric, hydrochloric, and acetic acid. It is insoluble in alkalis, appears to unite with baryta, is coloured green by ferric chloride. The alcoholic solution is not precipitated by lead-salts, platinic or mercuric chloride, nitrate of silver, or tincture of galls.

Colchiceine exerts, sometimes at least, a poisonous action when injected into the stomach. Oberlin states (Compt. rend. liii. 1202), that 0·1 grm. killed rabbits in 12 hours, and 0·05 grm. in a few minutes; but according to another account (Ann. Ch. Phys. [3] l. 114), even 0·5 grm. produced only temporary symptoms.

COLCHICINE. This alkaloïd, which is contained in all parts of the *Colchicum autumnale*, and probably also in other species of *colchicum*, was discovered by Pelletier and Caventou (Ann. Ch. Phys. [2] xiv. 69), who however regarded it as identical with veratrine. It was further examined by Geiger and Hesse, who first, in 1833, (Ann. Ch. Pharm. vii. 274) recognised its separate identity, and has been more recently investigated by Hübschmann (Arch. Pharm. [3] xcii. 330), Aschoff, *ibid.* lxxxix. 4), Bley (*ibid.* 18), and others.

Preparation.—1. The bruised seeds of colchicum are macerated with alcohol containing sulphuric acid; the extract is treated with lime, the filtered liquid saturated with sulphuric acid, and the alcohol expelled by distillation. The concentrated aqueous solution is then decomposed with carbonate of potassium; the precipitate is dried, and dissolved in absolute alcohol; the solution is decolorised with animal charcoal; the filtered liquid is evaporated at a gentle heat; and the alkaloïd thus obtained, is purified by repetition of the treatment with alcohol and animal charcoal (Geiger and Hesse).—2. According to Hübschmann, a larger product is obtained by exhausting the seeds with 3½ pts. alcohol of 90 per cent., then distilling off the alcohol, precipitating the residual liquid with carbonate of potassium; exhausting the dried precipitate with ether, and finally with sulphuric acid, to separate resin; and re-precipitating with carbonate of potassium.—3. Aschoff boils the comminuted seeds with water, neutralises the decoction with lime-water; filters after boiling, and evaporates to the consistence of an extract; then exhausts the extract with alcohol, continuing the process as long as the alcohol acquires thereby a bitter taste. The residue left after the distillation of the alcohol, is dissolved in water and precipitated with tannic acid; the precipitate is washed and pressed, then dissolved in alcohol, and digested with a sufficient quantity of recently precipitated ferric hydrate at 30° C.; lastly, the filtrate is evaporated, and the residue treated with absolute alcohol, which dissolves out the pure colchicine.—4. Polex exhausts the bruised seeds with a mixture of 4 pts. ether and 1 pt. alcohol, evaporates to dryness, dissolves the residue in water, and purifies the dissolved alkaloïd with animal charcoal.

Bley and Aschoff, obtained from the seeds, as a maximum, 0·2 per cent. of colchicine.

Colchicine may likewise be prepared by similar processes from the flowers, leaves, and bulbs of the plant.

Properties.—Colchicine crystallises from its alcoholic solution, on addition of water, in colourless prisms and needles: the alcoholic or ethereal solution leaves it, on evaporation, in the form of a transparent varnish (Geiger). According to other chemists, colchicine is always obtained as an amorphous yellowish white powder. It has a persistently bitter taste, not burning like that of veratrine; it is inodorous, and does not, like veratrine, excite sneezing. According to Geiger, it has a very faint alkaline reaction, reddening rhubarbarin, and bluing reddened litmus paper. According to Bley, Aschoff, and Hübschmann, on the contrary, it is perfectly neutral. It is permanent in the air.

The composition of colchicine has not been satisfactorily determined. According to Bley, it contains 55·0 per cent. C, 7·4 H, and 13·0 N, which he represents by the empirical formula $C^{27}H^{20}N^{3}O^{11}$, although his results agree better with $C^{30}H^{23}N^{3}O^{10}$, or $C^{15}H^{23}N^{3}O^{5}$. Aschoff found 55·2 C, 6·2 H, and 2·8 N, whence he deduces the formula $C^{23}H^{21}NO^{11}$. The great difference in the nitrogen determinations, and certain differences in the properties of the base, as observed by these two chemists, seem to show that they must have been operating, either upon different bases, or on the same in very different degrees of purity.

Colchicine dissolves with moderate facility in water, according to Hübschmann, in less than 2 pts. at 22° C.; this property distinguishes colchicine from veratrine, which is insoluble in water. It dissolves easily in alcohol, less easily in pure ether; at 20° C., in 18 pts. ether of specific gravity 0·74. Chloroform dissolves it readily, and withdraws it for the most part from the aqueous solution on agitation.

Colchicine, when strongly heated, melts and decomposes with intumescence (according to Bley, it volatilises at 112° C.). Strong nitric acid colours it deep violet or blue, quickly changing to olive-green and yellow; strong sulphuric acid colours it yellowish-brown, not violet, thus affording a distinction from veratrine. Phosphoric acid and hydrochloric acid colour even dilute solutions of colchicine distinctly yellow; chromic acid colours the solution green. Chlorine-water renders the solution turbid, and on subsequently adding ammonia, it assumes a yellowish-red colour. Colchicine is precipitated of a kermes-brown colour from its aqueous solution by tincture of iodine; yellow by dichloride of platinum, white by tannic acid, the last-mentioned precipitate being soluble in alcohol, acetic acid, and alkaline carbonates.

The statements of different chemists regarding the behaviour of colchicine with bases and acids do not agree. According to Aschoff, colchicine is converted by caustic alkalis into a brown resinous mass, soluble in water and alcohol; it unites with baryta and lime, but does not decompose alkaline carbonates. According to Bley, a solution of colchicine mixed with carbonate of soda, yields by evaporation a non-crystalline mass, free from carbonic acid (?).

According to Geiger, colchicine neutralises acids completely, forming extremely bitter salts, with rough irritating after-taste; some of them, the sulphate for example, are crystallisable and permanent in the air. They are very soluble in water and in alcohol, the aqueous solutions yielding with iodine and with tincture of galls the same reactions as the pure base; caustic alkalis precipitate the colchicine from concentrated, but not from dilute solutions of the salts. Bley and Aschoff did not succeed in preparing crystallisable compounds of colchicine with acids. The salts were acid, and soluble in water and alcohol, excepting the tannate, which is insoluble in water.

Physiological action.—Colchicine is poisonous, even small doses causing violent vomiting and purging; $\frac{1}{12}$th of a grain killed a cat in twelve hours. Tannin is said to be a good antidote. In cases of poisoning by colchicine, the alkaloïd may be detected by treating the stomach and intestines with strong alcohol, evaporating the liquid, and again treating the residue with alcohol, or with alcohol and ether, and again evaporating. Colchicine then remains as an amorphous yellowish mass, which exhibits the above-mentioned reactions with mineral acids, tincture of iodine, and tannic acid.

COLCHICUM AUTUMNALE. The root and seeds of this plant are used in pharmacy; according to Coindot, however, the flowers are more active and to be recommended for the preparation of a tincture.

The flowers, according to Reithner, contain colchicine in combination with tannic acid, also sugar, pectin, gum, fat, wax, and resin. The dried flowers, without anthers, yield 4·05 per cent. ash (*a*); the dried anthers alone yield 4·15 per cent. ash (*b*), containing in 100 parts:

	a.	*b.*		*a.*	*b.*
Potash	37·4	40·0	Silicic acid (anhydrous)	7·7	0·8
Soda	8·5	6·1	Carbonic ,,	22·3	22·5
Lime	4·3	2·6	Sulphuric ,,	3·7	6·2
Magnesia	3·0	6·5	Phosphoric ,,	10·6	14·4
Alumina	0·3	trace	Chlorine	1·5	0·5
Ferric oxide	0·5	0·2			

The ripe seeds collected in July contain in 100 pts., according to Bley: 0·2 colchicine, 5 glucose, and 6 fixed oil, together with resin, extractive matter, cellulose, and traces of veratric acid and gallic acid.

The fresh bulbs contain, according to the same authority, 0·2 per cent. colchicine, 0·3 sugar, 0·5 colouring matter, 29·0 starch, together with gallic acid, extractive matter, cellulose, &c. Colman found also 21 per cent. starch. The starch may be extracted from the bulbs by washing with water; after prolonged washing, it is perfectly pure and tasteless. (Handw. d. Chem. ii. [3] 153).

COLCOTHAR VITRIOLI, also called *Crocus Martis.*—The brown-red oxide of iron which remains after the distillation of sulphuric acid from sulphate of iron; it is used as a polishing powder.

COLLETIIN. A crystallisable bitter principle, obtained from *Colletia spinosa* (order *Rhamnaceæ*). It forms needles insoluble in cold water and ether, sparingly soluble in boiling water, easily in alcohol. It is contained in the alcoholic tincture of the plant, which, according to v. Martius, is used in Brazil as a remedy for intermittent fever. (Handw.)

COLLIDINE. $C^8H^{11}N$.—An alkaloïd found, together with many others, among the products of the dry distillation of animal substances and of coal. It was discovered by Anderson in 1855 (Phil. Mag. J. [4] ix. 145, 214), who obtained it from bone-oil, and was afterwards found by Greville Williams in the bituminous shale of Dorsetshire (Chem. Soc. Qu. J. vii. 97), in coal tar, and in the impure quinoline obtained by the dry distillation of quinine and cinchonine (Chem. Gaz., 1855, p. 308). It is isomeric with ethyl-phenylamine, ethyl-picoline, dimethyl-phenylamine, and xylidine.

Preparation.—1. The portion boiling above 170° C. of the mixture of volatile bases obtained from bone-oil (i. 625), is mixed with a considerable quantity of strong nitric acid, which acts very violently upon it, thereby acquiring a deep red colour, and on boiling evolves nitrous acid fumes and an odour of bitter almonds. The part boiling at 182° C. must be well cooled while being mixed with the nitric acid, to prevent explosion. The acid solution, when mixed with water, becomes turbid, from the separation of a reddish-yellow oil, which seems to be impure nitro-benzene; the acid solution is filtered through moist paper, and the filtrate is boiled for some time to expel the last traces of the neutral oils, then saturated with potash and distilled. The oil which passes over with the water is repeatedly rectified, and the portion boiling between 178° and 180° is collected. The part of the mixture of bases boiling above 170° contains a considerable quantity of phenylamine, which cannot be removed, either by repeated rectification or by recrystallisation of the oxalate; by the action of nitric acid it is destroyed, whilst the alkalis homologous with collidine remain undecomposed.—The part boiling between 172°—180°, when treated in this manner, yields, by distillation with potash, an oil which begins to boil at 160°, and is composed for the most part of lutidine; while the portion boiling above 180° yields an oil, the greater part of which goes over at 179°, and when rectified yields pure collidine. (Anderson.)—2. When the mixture of chinoline with other bases, which is obtained by the distillation of cinchonine with potash, is subjected to oft-repeated fractional distillation, the portion boiling between 177° and 182° C. yields, with solution of platinum, chloroplatinate of collidine. This salt may also be obtained from the fraction boiling between 182° and 187°, if another base mixed with it has previously been destroyed by means of nitric acid. (Gr. Williams.)

3. Gr. Williams mixes the naphtha obtained by the distillation of the bituminous shale of Dorsetshire with sulphuric acid; boils with water until all the tar is converted into resin, and all the pyrrol is removed; concentrates the liquid; neutralises with lime or potash, and distils; supersaturates the distillate with hydrochloric acid; removes the non-basic oil; then supersaturates the acid liquid with lime or potash, and distils. The distillate is freed from ammonia by washing with strong potash, dried by solid hydrate of potash, and fractionally distilled until liquids of constant boiling points are obtained. The small portion which passes over between 132° and 138° C. is lutidine mixed with a little picoline (from the mother-liquor of the chloroplatinate of lutidine, the double salt of picoline is obtained); the portion obtained between 149° and 155°, and between 177° and 182° is pure lutidine; and that which passes over between 227° and 258° is collidine.—4. The mixture of volatile bases obtained in like manner from coal-tar oil is treated, as in Anderson's process, with nitric acid, and subjected to repeated fractional distillation. The portion which distils between 150° and 155° C. is lutidine, and afterwards a small quantity of collidine passes over. (Gr. Williams.)

Properties.—Collidine is a colourless, oily liquid, having a strongly aromatic, not unpleasant odour. Specific gravity, 0·921; boiling point, 179° C. It forms white fumes when a glass rod moistened with hydrochloric acid is held over it. It is insoluble in *water*, but takes up a small quantity of that liquid, which it gives up again to hydrate of potassium. It dissolves readily in *alcohol*, *ether*, and *oils*, both fixed and volatile.

Collidine dissolves readily in *acids*, but does not neutralise them. It does not precipitate the salts of barium, calcium, magnesium, manganese, or nickel, but throws down alumina, chromic oxide, oxide of zinc, ferric oxide, and mercurous oxide from their solutions: it also precipitates nitrate of lead, but not the neutral acetate. (Anderson.)

Chloromercurate of Collidine is obtained as a white, curdy, flaky precipitate, and crystallises from hot water in needles. The *chloroplatinate*, $C^8H^{11}N.HCl.PtCl^2$, forms orange-yellow flakes. (Anderson.)

Ethyl-collidine, $C^{10}H^{15}N = C^8H^{10}(C^2H^5)N$.—The hydriodate of this base is obtained as an oily liquid by heating collidine to 100° C. with iodide of ethyl. On decomposing it with nitrate of silver, removing the excess of silver by hydrochloric acid, and mixing the filtered liquid with dichloride of platinum, the *chloroplatinate*, $C^{10}H^{15}N.HCl.PtCl^2$ is obtained, as a finely-divided, crystalline, sparingly soluble precipitate (Anderson, Phil. Mag. [4] ix. 221).

COLLINIC ACID. $C^6H^4O^2 = \left.\begin{matrix}C^6H^3O\\H\end{matrix}\right\}O$. (Fröhde [1860], J. pr. Chem. lxxx. 344).—An acid belong to the aromatic series $C^nH^{2n-8}O^2$, found among the products of the oxidation of the albuminoïdal substances, and of gelatin. To obtain it, the mixture of acids produced by oxidising gelatin with chromic acid is saturated with carbonate of sodium, and evaporated to drive off the neutral volatile bodies; the nearly dry salts are decomposed by sulphuric acid; and the solid acid thereby separated is filtered and washed. If the residue be then treated with a small quantity of boiling water, the greater part of the collinic acid remains in fused reddish masses (about 0·96 grm. collinic acid from 1 kilogrm. gelatin), while the other acids, especially the benzoic acid, dissolve completely, together with a small portion of the collinic acid. By recrystallisation from water, it may be obtained in small crystals having a prismatic aspect.

Collinic acid has a sour, pungent taste; dissolves sparingly in boiling water, easily in ether. When heated with water, it melts at 97° C, and then solidifies at 93° or 94°; in the dry state, it does not melt till heated somewhat above 100°. On cooling, is solidifies to a waxy mass generally having a radiate texture. At a higher temperature, it sublimes. When set on fire, it burns with a bright but smoky flame. Boiled with carbonate of sodium, it yields humoïd flakes. Heated with hydrate of potassium, it decomposes, but does not appear to yield any volatile acids.

Collinic acid is a strong acid, dissolving in caustic alkalis, and decomposing carbonates. It forms both neutral and basic salts. The silver-salts decompose with facility.

A solution of *collinate of ammonium* gives off ammonia and becomes acid on boiling; acid vapours, however, escape at the same time. The *barium-salt*, $2C^6H^3BaO^2$ + aq., is crystalline, easily soluble in water, gives off water of crystallisation when heated, melts and blackens at a higher temperature. The *ferric salt* is a light, yellowish-red precipitate, which dissolves with blood-red colour on addition of a small quantity of acid. The *neutral silver-salt*, $C^6H^3AgO^2$, is obtained in crystalline scales by precipitating the ammonium-salt with nitrate of silver, dissolving the precipitate in water, and evaporating over oil of vitriol. The mother-liquor when evaporated gives off acid and yields grey granules of a basic salt, $Ag^2O.2C^6H^3AgO^2$; by continued heating of the solution, the silver-salt is reduced.

An acid isomeric, if not identical with collinic acid, is produced by oxidising coal-tar naphtha with dilute nitric acid (De La Rue and Müller, Chem. Soc. Qu. J. xiv. 54), or sulpho-benzolic acid with chromic acid. (Church, *ibid.* 53.)

COLLINIC ALDEHYDE. *Hydride of collyl.*—This compound occurs, according to Fröhde (J. pr. Chem. lxxx. 325), among the neutral volatile products of the oxidation of the albumoïds, and of gelatin; it appears to have been previously noticed by Schlieper and Guckelberger. It is probably C^6H^6O (isomeric with phenic acid). It has not yet, however, been obtained pure, especially not free from hydride of benzoyl. It is a colourless viscid oil, smelling somewhat like oil of cinnamon, and turning yellow from oxidation when exposed to the air. By prolonged boiling with potash-ley, it is converted into collinic acid. By continued contact with ammonia, it is converted into a white crystalline substance, probably the homologue of hydrobenzamide.

According to Schlieper (Ann. Ch. Pharm. lix. 22), this oil having the odour of cinnamon is converted by the action of dry chlorine, with elimination of hydrochloric acid, into a white substance which is insoluble in ether, and when heated with potash-ley forms a blood-red volatile oil; the potassium-salt, on addition of an acid, emits the odour of phenic acid.

COLLODION (from κολλώδης, glutinous). A solution of pyroxylin (gun-cotton) in ether. The solubility of this substance in ether, varies considerably according to the mode of its preparation; the most explosive kinds are by no means the most soluble (see PYROXYLIN). The best mode of obtaining pyroxylin, for the preparation of collodion, is to mix 16 pts. of nitrate of potassium with 12 pts. of common and 12 pts. of fuming oil of vitriol; immerse in this mixture, as soon as it is made, 1 pt. of cotton wool, stir it about for five minutes, and then wash it well with water.

To prepare collodion, pyroxylin obtained in the manner just described is shaken up with 16 pts. ether, in a bottle which can be closed. 1 or 2 pts. of absolute alcohol are added after a while, and the vessel shaken at intervals, till the solution is complete. Lassaigne pours 26 pts. of ether on 1 pt. of pyroxylin, and mixes the resulting jelly with 18 pts. more of ether. According to other methods, 1 pt. of pyroxylin is treated with from 20 to 120 pts. of ether, and from 4 to 16 pts. of alcohol. The solution obtained by either of these methods is left to stand till the undissolved parts have settled down.

Pyroxylin is said also to be rendered perfectly soluble in ether by moistening it with acetone.

Collodion is a clear colourless gummy liquid, insoluble in water and alcohol, but soluble in ether; when exposed to the air, it soon dries up, leaving a transparent or translucent residue, which becomes strongly electric by friction, explodes less easily by heat, pressure, or percussion than flocculent pyroxylin, and is soluble in ether containing alcohol and in strong acetic acid.

When the ethereal solution is suffered to evaporate in a thin film, it dries up quickly to a thin transparent membrane, which possesses great adhesiveness, is tolerably impervious to air, and is not dissolved either by water or by alcohol. These properties render collodion very useful for a variety of purposes. It is employed with great advantage in surgery to form an air-tight covering for wounds and burns; when spread over an incised wound, it greatly promotes the healing by drawing the edges of the wound together, the film of collodion contracting strongly as the ether evaporates. As the collodion film is rather solid, and has but little elasticity, it has been recommended to melt 2 grms. of Venice turpentine with 2 grms. castor oil and 2 grms. of white wax, mix the fused mass with 6 grms. of ether, and add the whole to 140 grms. of collodion.

Collodion is also used as an envelope for caustic substances, in order to confine their action exactly to the desired spot. Pills may be coated with it, so as to render them tasteless, and wood, paper, and other fabrics may be rendered water-proof by being covered with it.

Collodion is also largely used in photography. A thin layer of the solution, mixed with iodide, bromide, or chloride of potassium, or ammonium, is spread uniformly over a glass plate, then treated with a solution of nitrate of silver to form the sensitive film. It appears to be essential to use anhydrous ether and alcohol for the solvent, in order to insure uniform evaporation.

Another application of collodion is for making balloons. For this purpose, a solution of collodion, not too thick, is poured into a flask of suitable dimensions, which is turned about to spread the liquid uniformly over it, and then inverted to allow the excess to run out. The ether is now evaporated from the film of liquid which adheres to the glass, by blowing into the flask with a pair of bellows, whereby the collodion is left in the form of a thin membrane on the surface of the glass. To remove it, the edges of the film are loosened from the glass, a glass tube of suitable character is inserted into the neck of the flask, so that the balloon may adhere to it, and the air is slowly drawn out with the mouth; the balloon then detaches itself from the vessel, contracts, and is easily withdrawn through the neck. It must be immediately blown out and tied at the neck, so that it may dry in the distended state. Small and thin balloons do not diminish much in volume as they dry; but larger ones contract strongly: this contraction may, however, be prevented by drying the balloon in warm air. Collodion balloons may be made much lighter than those of gold-beater's skin, so that much smaller ones will rise in the air when filled with detonating gas (2 vol. H and 1 vol. O). They may be made so thin that a balloon containing 100 cubic centimetres shall weigh only 0·03 grms. when empty, and 0·04 when filled with hydrogen; now the weight of an equal volume of air is 0·13 grms., consequently such a balloon will rise rapidly in the air. Hydrogen diffuses quickly through their pores. Collodion balloons become strongly electric by slight friction; when very thin, they exhibit beautiful interference-colours. (Handw. d. Chem. ii. [2] 158).

COLLYL, HYDRIDE OF. See Collinic Aldehyde.

COLLYRITE. A hydrated silicate of aluminium, $2Al^4O^6.SiO^2 + 10aq.$, found at Esquerra in the Pyrenees, near Schemnitz in Hungary, and near Wessenfels in Saxony. It is white, very soft, earthy, unctuous to the touch, adheres strongly to the tongue. In water it becomes transparent and crumbles to pieces: it dissolves in acids and the solution yields a jelly by evaporation (Gm. iii. 411.)

COLOCYNTHIN. A bitter substance contained in the pith or pulp of the fruit of *Cucumis colocynthis* (bitter apple), a plant growing wild in the Grecian Archipelago, also in Egypt, and other parts of North-eastern Africa. It has been examined by Vauquelin (J. Phys. lxxxiv. 338), Braconnot (J. Pharm. x. 416), Herberger

(*Buchner's Repert.* xxxv. 368), **Bastick** (Pharm. J. Trans. x. 289), and lastly by **Walz** (Arch. Pharm. xcvi. 241; xcix. 338), who regards it as a glucoside = $C^{56}H^{84}O^{23}$.

It is prepared from the pulp of the fruit separated from the seeds. Vauquelin exhausted the pulp with cold water, and evaporated the extract, the colocynthin then separating in oily drops, which solidified on cooling. **Lebourdais** (Ann. Ch. Phys. [3] xxiv. 58) precipitates the aqueous extract with neutral acetate of lead, and treats the filtered liquid with animal charcoal, which takes up both the colouring matter and the bitter principle. The charcoal is then washed with water. As long as the liquid which runs through it acquires a bitter taste, nothing but pure colocynthin is dissolved; and on again precipitating it with animal charcoal, boiling the charcoal with alcohol, and leaving the solution to evaporate, the colocynthin separates in small warty groups. Walz exhausts the fruit with alcohol of 0·840; evaporates; dissolves the extract in water; precipitates the filtrate with neutral and with basic acetate of lead; removes the lead from the filtered liquid by sulphuretted hydrogen; and precipitates the colocynthin by tannic acid. The precipitate, which becomes resinous on heating the liquid, is dissolved in alcohol; the tannic acid is precipitated with basic acetate of lead; the filtrate, freed from lead, is heated with animal charcoal; the liquid is again filtered and evaporated; and the dry residue exhausted with ether, which leaves the colocynthin undissolved.

Colocynthin is intensely bitter, and acts as a drastic purgative. It is soluble in water, alcohol, and ether. The aqueous solution is precipitated by chlorine; it also yields, with acids and with deliquescent salts, a viscous precipitate insoluble in water. The solution is also precipitated by acetate of lead and many other metallic salts.

Colocynthin boiled with acids is resolved, according to Walz, into sugar (7·7 per cent.) and **colocynthein**, $C^{44}H^{64}O^{13}$, which remains as a resinous mass, and may be purified by washing with water, solution in absolute ether, and evaporation.

COLOCYNTHITIN. A body contained, according to **Walz** (N. Jahrb. Pharm. ix. 225), in the alcoholic extract of bitter apple (see CUCUMIS). When this extract is treated with water, colocynthitin remains undissolved; and on treating this residue with ether, digesting the solution with animal charcoal, evaporating the filtrate, exhausting with hot absolute alcohol, and leaving the filtered liquid to cool, colocynthitin separates in white microscopic crystals. It is soluble in ether.

COLOMBIC ACID. An acid obtained by **Bödecker** (Ann. Ch. Pharm. lxix. 47), from colombo-root, the root of *Menispermum palmatum*, L., *Cocculus palmatis*, Dec. To prepare it, the alcoholic extract of the root is exhausted with water or lime-water, and the solution treated with hydrochloric acid. Colombic acid is then precipitated in white amorphous flakes, which are strongly acid, nearly insoluble in cold water, very soluble in alcohol, sparingly soluble in cold ether. By the evaporation of its alcoholic solution, it is obtained in the form of a yellow varnish.

The alcoholic solution of colombic acid is not precipitated by acetate of copper, but yields with neutral acetate of lead a copious white precipitate, which, when dried at 130° C. contains 30·53 per cent. lead oxide, agreeing nearly with the formula $3Pb^2O.2C^{42}H^{44}O^{12}$. Dried at 100° C., it contains in addition $5H^2O$.

The acid itself, dried at 115° C., gave by analysis 66·64 per cent. C, and 6·29 H, agreeing nearly with the formula $C^{42}H^{46}O^{13}$, or $C^{42}H^{44}O^{12}.H^2O$.

COLOMBIN. *Colombo Bitter.* $C^{21}H^{22}O^{7}$. (**Wittstock** [1830], Pogg. Ann. xix. 298.—**Liebig**, *ibid.* xxi. 30.—**Bödecker**, Ann. Ch. Pharm. lxix. 39.)—A neutral substance which constitutes the active principle of colombo root. Bödecker prepares it by exhausting the root with alcohol of 75 per cent., drying the extract as completely as possible, dissolving it in water, agitating the solution several times with an equal volume of ether, decanting the ethereal liquid with a siphon, filtering, and evaporating off the greater part of the ether. The colombin then crystallises out, and is purified by rinsing it with cold ether, pressing it between bibulous paper, dissolving it in boiling absolute ether, and concentrating the solution to one-fourth of its bulk. The greater part of the colombin then separates out quite white, the rest remaining dissolved in the ether, together with the fat contained in the root. To free the colombin entirely from fat, it must be repeatedly crystallised from ether; when quite pure it will dissolve in acetic acid without separation of oil-drops.

Colombin crystallises in colourless prisms belonging to the trimetric system. Observed combination, $\infty P . \infty \bar{P} \infty . \infty \breve{P} \infty . \bar{P} \infty$. Inclinations of the faces, $\infty P : \infty P = 125° 30'$; $\infty P : \infty \bar{P} \infty = 152° 45'$; $\infty P : \infty \breve{P} \infty = 117° 15'$; $\bar{P} \infty : \bar{P} \infty = 176° 19'$; $P \infty : \infty \breve{P} \infty = 123° 39·5'$; $\infty P : \bar{P} \infty = 119° 31'$. The faces are brilliant, but the crystals do not cleave in any direction (**G. Rose**, Pogg. Ann. xix. 441). Colombin is inodorous, very bitter, and perfectly neutral to vegetable colours. It melts at a gentle heat. It dissolves but sparingly in cold water, alcohol, and ether, but imparts to them a strong bitter taste. Boiling alcohol of specific gravity 0·835 dissolves from $\frac{1}{40}$

to $\frac{1}{80}$ of its weight of colombin. It dissolves to a small amount in volatile oils, and more freely in potash, whence it is precipitated by acids in its original state. Acetic acid dissolves it and deposits it in the crystalline state on evaporation. Strong sulphuric acid dissolves it with orange colour, gradually changing to deep red, and on adding water to the solution, brown flakes are deposited. Solutions of colombin are not precipitated by any metallic salts or by tincture of galls.

Colombin yields, according to the mean of Bödecker's analyses, 65·20 per cent. C and 5·98 H, the above formula requiring 65·3 C, 5·7 H, and 29·0 O. It does not form any definite compound, so that its atomic weight cannot be determined.

COLOMBO ROOT. The root of *Cocculus palmatus*, Dec., contains colombin, berberine, colombic acid (probably as colombate of berberine), besides starch, colouring matter, &c. The colombic acid and berberine may perhaps be formed from colombin by addition of the elements of ammonia (Bödecker):

$$\underset{\text{Colombin.}}{4C^{21}H^{22}O^7} + 2NH^3 = \underset{\text{Berberine.}}{2C^{21}H^{19}NO^4} + \underset{\substack{\text{Colombic}\\\text{acid.}}}{C^{42}H^{44}O^{15}} + 5H^2O.$$

The root acts with violence on the animal organism; a grain of the dry extract prepared with ether and freed by water from fat and wax, killed a rabbit when introduced into a wound. This active property appears to be due to the colombin. (Buchner.)

COLOPHANE. A constituent of icica resin (*q. v.*), containing, according to Scribe (Compt. rend. xix. 129), $C^{20}H^{30}O^2$. It is yellow, amorphous, easily soluble in alcohol, melts above 100° C., is insoluble in aqueous alkalis, and reacts neutral.

COLOPHENE. $C^{20}H^{32}$ or $C^{40}H^{32}$. (H. Deville, Ann. Ch. Phys. [2] lxxv. 66; [3] xxvii. 85.)—A hydrocarbon polymeric with oil of turpentine, obtained by distilling that oil with strong sulphuric acid, or by distilling hydrate of turpentine-oil with phosphoric anhydride. In either case, terebene ($C^{10}H^{16}$) passes over first; afterwards, when the heat rises above 210° C. colophene distils; it is purified from sulphur and a substance resembling colophony by repeated rectification, at last over antimonide of potassium. It may also be obtained by the rapid distillation of colophony, the product being purified in like manner.

Colophene is an aromatic oil, colourless by transmitted light, and exhibiting by reflected light a dark indigo-blue iridescence. Specific gravity, 0·940 at 9° C., 0·9394 at 25°. Boiling point between 310° and 315°. Vapour-density = 11·13 (probably only twice as great as that of oil of turpentine, therefore = 9·526). Refracting power = 1·517 (Becquerel and Cahours), 1·5212 (Deville). It has no action on polarised light.

Colophene absorbs *chlorine gas* without evolution of hydrochloric acid, becoming hot, and changing to a resin like colophony, which separates in yellow spherules from its solution in absolute alcohol. If, when the absorption of chlorine has ceased, the product be heated to fusion in the stream of chlorine, a large quantity of hydrochloric acid is evolved, and Deville's *chlorocolophene* = $C^{20}H^{24}Cl^8$ is formed, which however still contains a resin removable by alcohol, and when distilled, gives off hydrochloric acid, yields a distillate of colophene and hydrochlorate of colophene, and leaves charcoal.

Hydrochlorate of Colophene.—Colophene absorbs hydrochloric acid gas, with rise of temperature, and acquires an indigo-colour. The hydrochlorate gives up nearly all its hydrochloric acid when treated with chalk, and when distilled with baryta, yields Deville's *colophilene* = $C^{20}H^{32}$, which does not exhibit the dichroism of colophene, and has a refracting power for light = 1·5175. (Deville, Becquerel, and Cahours, Pogg. Ann. li. 427–433.)

Colophene from Camphor. (Claus, J. pr. Chem. xxv. 266.—When camphor is distilled with an equal weight of iodine, hydriodic acid is evolved, camphin passes over at 180° C., and charcoal, iodine, campho-creosote and colophene remain behind (i. 728). On increasing the heat, the two latter substances distil over as a bluish-green oil, which is deprived of its creosote odour by agitation with potash, but cannot be obtained quite pure, even by distillation over lime and finally over potassium.

It is a thick, yellowish oil, with violet iridescence, having a high boiling point, a mild taste, and an odour of violets, and burning with a bright fuliginous flame. It is perhaps identical with colophene from oil of turpentine or from colophony.

It is not soluble in *water* or in weak *alcohol*, but dissolves in *ether*, *oil of turpentine*, *rock-oil*, and *camphine*. When 2 drops of it are dissolved in 2 drachms of alcohol, the solution, after agitation with animal charcoal, exhibits a fine dark blue colour by reflected light.

COLOPHILENE. The hydrocarbon $C^{20}H^{32}$ obtained from Deville's hydrochlorate of colophene (*vid. sup.*)

COLOPHOLIC ACID of Unverdorben; *γ-resin of Colophony* of Berzelius. The constituent of colophony which is least soluble in alcohol, and is produced by the action of heat on pinic acid. It is therefore present in colophony in variable quantity, according as that substance has been more or less heated during fusion; the darker varieties contain about one-tenth. Colopholic acid is said to be likewise produced when pinic acid is distilled till a third of it has passed over.

Colopholic acid is brown, sparingly soluble in alcohol of 67 per cent., more readily in presence of pinic acid. It has a stronger affinity for bases than pinic acid; nevertheless the colopholates exactly resemble the pinates.

COLOPHONIC ACIDS. The resinous acids, pinic, pimaric, sylvic and colopholic, which are present in colophony.

COLOPHONITE. A variety of garnet, so called from its brown colour, resinous lustre, and easy fusibility. (See GARNET.)

COLOPHONONE. $C^{11}H^{18}O$. (Schiel, Ann. Ch. Pharm. cxv. 96).—An oil occurring among the more volatile products of the dry distillation of colophony; it is separated by fractional distillation. It is colourless, mobile, highly refractive, of specific gravity 0·84, boils at 97° C.; vapour-density about 5·1. When heated above its boiling point in a close vessel, it turns brown, and emits an odour of peppermint. It mixes with sulphuric acid, and on addition of water, a green oil separates, having an odour of thyme and rosemary. Hydrochloric acid acts in like manner; nitric acid converts it into a resin. With potassium, it gives off gas, and is converted into a brown mass, subsequently turning yellow.

COLOPHONY. *Rosin, Colophonium, Colophane, Arcanson, Brai sec, Geigenharz.*—The resinous substance which remains when turpentine or pine-resin is heated till the water and volatile oil are expelled. It is for the most part a mixture of several resinous acids, viz., pinic acid (the α-resin of Berzelius), which forms the principal part, sylvic acid (β-resin), and colopholic acid (γ-resin), sometimes also pimaric acid. These acids, which are mixed in various proportions, are all isomeric, their common formula being $C^{20}H^{30}O^2$ or $C^{40}H^{30}O^4$. They are perhaps formed by oxidation of turpentine oil:

$$2C^{10}H^{16} + O^3 = C^{20}H^{30}O^2 + H^2O.$$

Colophony is either pale yellow and transparent (*C. album*) or brownish-yellow and translucent (*C. commune*), according to the degree of heat to which it has been exposed. By distillation with steam under a pressure of about ten atmospheres, it may be obtained very nearly colourless (*Hunt and Pochin's Patent*, 1858, No. 925). It has a vitreous lustre, is brittle in the cold, has a conchoïdal fracture, and yields a yellowish powder. Its specific gravity varies from 1·07 to 1·08. It is insoluble in water, but dissolves easily in alcohol, ether, wood-spirit, and oils both fixed and volatile. Rock-oil dissolves only a portion of it; the undissolved part is said to be identical with pinic acid altered by the action of the air. Nitric acid dissolves and decomposes it at the same time.

Colophony, being a mixture of acids, unites with bases. The compounds which it forms with the alkalis are soaps soluble in water. It is easily saponified either by caustic alkalis or by their carbonates.

Colophony softens at 69° or 70° C. and melts at 135°. At a higher temperature it gives off volatile oils, acquiring a darker colour, and yields colopholic acid. When quickly heated in a retort, it distils partly undecomposed, partly resolved into gases, volatile oils, viz. Deville's terebene and colophene, and perhaps other hydrocarbons, finally yielding viscid oils, with a small residue of carbonaceous matter. When the distillation is performed on the large scale in cast iron retorts, the gases evolved in the first half of the distillation contain, besides the constituents of the air, 15 per cent. carbonic anhydride, 11·5 carbonic oxide, 5·9 ethylene and tetrylene; at a higher temperature, the oxygen disappears, the proportion of carbonic anhydride increases, and lastly a small quantity of marsh-gas is formed. The first portion of the liquid distillate is a yellow, mobile, strong-smelling liquid, known in commerce as *essence of rosin* (*vive essence, Harzessenz*); it yields by fractional distillation, first colophonone (*q. v.*), and afterwards an optically indifferent camphene (i. 724), boiling at 160° C., having the odour and other properties of oil of turpentine, and perhaps identical with Deville's terebene. At a later stage of the dry distillation, a viscid fluorescent oil passes over, called *rosin-oil* or *paraffine-oil*, which, after being treated with quick-lime, corresponds in composition to the formula $C^{30}H^{40}O$. After rectification, it no longer exhibits fluorescence, and if again treated with lime, gives the formula $C^{30}H^{28}O$ (Schiel, Ann. Ch. Pharm. cxv. 96). At a red heat, colophony yields a mixture of gases burning with a very bright flame, which it has been attempted, though without much success, to use as an illuminating gas.

Colophony is extensively used in making varnishes and cements, in the caulking of ships, in the preparation of plasters and ointments, and as a reducing agent in the soldering of metals. Large quantities are consumed in the manufacture of yellow soap. A well known use of it is for covering the bows of violins, to prevent the bow from slipping over the strings without producing vibration. Of the products obtained by the dry distillation of colophony, the more volatile oil is used in place of turpentine-oil, the more viscid rosin-oil for soap-making, and for lubricating cartwheels, &c. (Handw. d. Chem. i. [3] 160.)

COLORIMETER. An instrument for measuring the depth of colour in a liquid by comparison with a standard liquid of the same tint. The comparison is made either by varying the depth of the stratum of liquid under examination till it exhibits the same intensity of colour as the normal liquid, and then measuring the depth of the stratum, — or by diluting the stronger-coloured liquid with water, till equal columns of the two exhibit the same depth of colour.

COLORIN. A colouring matter obtained by Robiquet and Colin from madder, since shown to be impure alizarin.

COLOSTRUM. The milk of mammalia secreted in the first few days after parturition, before the access of milk-fever. It is distinguished from ordinary milk by containing a larger amount of solid constituents, also a larger proportion of fat, casein, and milk-sugar. (See MILK.)

COLOUR. (See LIGHT).—A table of oil painters' colours, with notices of their chemical and artistical qualities, drawn up by W. Linton, is given in *Ure's Dictionary of Arts, Manufactures, and Mines*, vol. i. p. 803; see also *Chimie des Couleurs pour la Peinture à l'Eau et à l'Huile*, par. J. Lefort. 12mo. Paris, 1855.

COLOURING MATTERS. This term is usually restricted to coloured compounds of vegetable or animal origin, sometimes more especially to such as exist ready formed in the bodies of plants and animals, or are easily formed from them by natural processes, such as oxidation or fermentation. Accordingly, it would be applied to such bodies as indigo, Indian yellow, and carmine, rather than to compounds like aniline-purple or murexide, which are formed by complicated artificial processes. This restriction of the term must not, however, be regarded as absolute, since many artificial organic coloured compounds resemble the natural colouring matters in their most essential properties, especially in those which render them available as dyes.

Colouring matters occur in all the organs of plants and animals. Many are obtained from roots, as alkanet, turmeric, madder, &c.; from the stems, as from sandal-wood, log-wood, Brazil-wood, &c.: leaves, flowers, fruits, and seeds are also rich in colouring matters. Of some insects, as the cochineal-insect, the entire substance is used as a dye; certain liquids of the animal organism, as the blood and bile, are also strongly coloured. Colouring matters rarely exist either in plants or animals in the separate state; indeed their separation is often a matter of considerable difficulty. Many do not exist ready formed in plants, but are produced from originally colourless compounds by oxidation or fermentation; in some instances, also, by the action of oxygen in presence of alkalis.

Colouring matters are for the most part either red, yellow, or blue, the last being the least numerous. Only one green colouring matter occurs in nature, namely, the chlorophyll of leaves.

Colouring matters have generally a saccharine and somewhat harsh taste; they are inodorous, some of them, as indigotin and alizarin, crystallise readily; others are of a resinous character. Many are volatile, as alizarin; but they must always be distilled with caution, as a heat of 150° C. is often sufficient to decompose them.

All colouring matters are affected by light, mostly absorbing oxygen under its influence, and becoming more or less decolorised. The green colour of chlorophyll on the contrary requires the presence of light for its development.

Many colouring matters are soluble in water, others only in alcohol, ether, or volatile oils; in some cases, the presence of an acid facilitates the solution, although the colouring matter may not actually possess basic properties, *e.g.* hæmatosin, indigotin, alizarin, purpurin; others on the contrary, as carthamin and santalin, dissolve readily in alkalis.

The tint of colouring matters is modified in various degrees, and sometimes completely destroyed, by chemical reagents. The alkalis turn the naturally red colour of litmus to blue, many vegetable blue colours to green, and the yellow of rhubarb or turmeric to brown. The alkaline compounds of alizarin are of a rich violet colour, though alizarin itself is reddish yellow. All colouring matters are decomposed by concentrated alkalis.

Many metallic oxides, *e.g.* alumina and oxide of tin, form chemical compounds with colouring matters. Such compounds are called lakes. Many salts also, especially those of aluminium, iron, and tin, act upon colouring matters so as to form compounds by means of which the colouring matter is fixed upon organic tissues; such substances are called mordants.

Porous substances, especially animal charcoal, absorb colouring matters without decomposing them; thus, if an infusion of logwood be decolorised by filtration through animal charcoal, the colouring matter may be recovered by treating the charcoal with a weak alkaline ley.

All organic colouring matters are destroyed by chlorine in presence of water, the action consisting, in most cases, of a direct oxidation of the colouring matter, by oxygen set free by the decomposition of water. Sometimes, however, the chlorine takes hydrogen from the colouring matter itself and partly replaces it.

Oxygen in the nascent state likewise acts as a decolorising agent, when derived from other sources; thus, peroxide of hydrogen quickly destroys the colour of organic bodies, and indigo is bleached by nitrous acid.

Sulphurous acid decomposes and bleaches many colouring matters, sometimes by abstracting oxygen, sometimes by uniting with the colouring matter and forming a colourless compound. It is a valuable bleaching agent in many cases, especially for silk and wool, because it destroys the colouring matter without acting on the tissue, whereas chlorine would act very injuriously upon it. Fruit stains are easily removed from linen by washing with a weak solution of sulphurous acid, or by holding the moistened cloth over burning sulphur; care must be taken, however, to wash it well afterwards, or the sulphuric acid produced in the reaction will destroy the fibre.

Many reducing agents, such as nascent hydrogen, sulphydric acid, alkaline sulphides, ferrous salts, &c., decolorise colouring matters in such a manner that the colour is restored by mere exposure to the air; thus, blue indigo is converted into white indigo by the action of these bodies, but recovers its blue colour by atmospheric oxidation. The action consists either in a direct deoxidation of the colouring matter, or in a combination of the colouring matter with hydrogen derived from the decomposition of water. Thus white indigo, C^8H^6NO, is formed from blue indigo, C^8H^5NO, by addition of 1 at. hydrogen. (*Traité de Chimie générale, par Pelouze et Frémy*, 2^{me} ed. v. 492; *Ure's Dictionary of Arts, Manufactures, and Mines*, i. 806.)

COLUMBITE. See NIOBITE.

COLUMBIUM or **NIOBIUM.** A metal originally discovered in columbite from Massachusetts, and since shown to exist in the tantalite (or rather columbite) of Bodenmais in Bavaria, also in Samarskite, pyrochlore, wöhlerite, euxenite, and a variety of pitchblende from Satersdalen in Norway. It was discovered by Hatchett in 1801. Wollaston erroneously supposed it to be identical with tantalum, the metal discovered a short time afterwards by Ekeberg in Finland tantalite. This opinion was long received as correct, and columbium is even now spoken of in most Manuals of Chemistry as identical with tantalum; but the researches of H. Rose have shown that this supposed identity does not exist. In short, columbium is identical, not with tantalum, but with Rose's niobium (*q. v.*)

COMBUSTION. This term properly denotes the development of light and heat accompanying chemical combination. It is sometimes used as synonymous with *inflammation*, which, however, is better restricted to those cases of combustion in which the products are gaseous, in other words, in which flame is produced. *Ignition* is the incandescence of a body produced by extrinsic means, without change of its chemical constitution.

The earlier chemists, feeling daily the necessity of fire to human existence, and astonished at the changes which this power seemed to produce in charcoal, sulphur, the metals, and other bodies, regarded combustion as the grand and essential phenomenon of chemistry. At the beginning of the eighteenth century, Stahl, of Prussia, by applying the views of Albertus Magnus and Becher respecting combustion to the whole collection of facts discovered by himself and others, and uniting them into a connected whole, laid the foundation of the first system of chemistry. This system received the name of the "Phlogistic Theory," because Stahl assumed that all combustible bodies contain one and the same principle of combustion called *Phlogiston*, the escape of this substance from a heated combustible body being supposed to produce the phenomenon of combustion or fire, and its addition to a burnt body to restore the combustibility of that body: thus, phosphorus was regarded as a compound of phlogiston and phosphoric acid; lead of phlogiston and lead-earth or calx of lead, the substance now called oxide of lead. When a calx or earth was reduced to the metallic state by heating it with charcoal (a body rich in phlogiston), it was supposed that the burnt body took phlogiston from the charcoal, and was thus restored to the combustible state.

An obvious defect of the phlogistic theory was that it took no account of the essential part which the air plays in all ordinary cases of combustion, a fact suggested by common experience, and fully demonstrated by the discoveries of Scheele, Cavendish, and Priestley. Moreover it had long been known that many combustible bodies, the metals for example, do not lose, but gain weight when burnt; and towards the end of the eighteenth century Lavoisier showed, by experiments on combustion, made with a degree of accuracy in the determination of weights and volumes, quite unknown before his time, that whenever a body burns in the air or in oxygen gas, the oxygen enters into combination with the burning body, and the weight of the product is exactly equal to the sum of the weights of the combustible body burnt and of the oxygen consumed. It was also shown that, in the reduction of a metal from its calx (or oxide) by charcoal, the latter body takes oxygen from the calx and leaves the metal in the free state. In short, wherever the phlogistic theory supposed that phlogiston was removed from a body, Lavoisier's experiments showed that oxygen was taken up, and wherever, according to the former theory, phlogiston was supposed to be added, Lavoisier showed that oxygen was removed. This system of chemistry, called the "Antiphlogistic Theory," did not, however, meet with immediate acceptation from the majority of chemists, the advocates of the phlogistic system maintaining that the increase of weight of metals and other bodies in burning might be explained by abscribing to phlogiston a principle of levity,—in other words, a tendency to recede from the earth instead of falling towards it, as ponderable bodies do. Such an assumption, however improbable in itself, would of course suffice for its immediate purpose; that is to say, of accounting for the increase in weight of a body by loss of phlogiston; but the explanation thus afforded took no account of the oxygen, which Lavoisier had shown to be abstracted from the air and added to the burning body. Accordingly, as experiments were multiplied, and it was shown that in all cases of combustion, the weight of the product was equal to the weights of the combining bodies taken together, the phlogistic theory gradually lost its hold on the minds of chemists, and was ultimately abandoned.

At the time of Lavoisier, attention was chiefly directed to combustions taking place in the air or in oxygen gas, and to the reduction of metallic oxides by hydrogen or carbon. Chlorine also, then called *oxymuriatic acid*, was supposed to contain oxygen; bromine and iodine were not known. Accordingly it was natural that oxygen should be regarded as essentially the supporter of combustion, the bodies which burned in it being called combustibles. Afterwards, when chlorine was shown to be an elementary substance, and when bromine and iodine were discovered, and metals, &c., were found to burn in their vapours, the term supporter of combustion was extended to all substances capable of forming vapours in which others can burn; thus, when copper-foil burns in sulphur vapour, the sulphur may be called the supporter, and the copper the combustible. But since the same substance may act sometimes as a combustible, sometimes as a so-called supporter,—*e. g.* sulphur as a combustible with oxygen, as a supporter with metals,—the distinction has gradually become obsolete.

The development of heat and light in combustion was attributed, on Stahl's theory, to the escape of phlogiston. The antiphlogistic theory, by dwelling chiefly on the ponderable substance produced by the combustion, and the relation between its weight and those of the combining bodies, tended rather to divert attention from the attendant phenomena of light and heat, and, indeed, was somewhat reproached by the adherents of the older theory for not rendering a sufficient account of those phenomena. Lavoisier attributed the heat accompanying combustion to the separation of the latent heat of the oxygen gas; and attempts have been made to extend this mode of explanation to all cases of chemical combination, in which gaseous or liquid substances pass to the solid state. This, however, will not account satisfactorily for the more intense evolution of heat in combustions and other combinations: for the latent heat of gases and liquids is small in comparison with such developments of heat. Moreover, in many instances, the combination is not attended with condensation; *e. g.* in the combustion of charcoal or sulphur in oxygen gas, and of hydrogen in chlorine gas; or again, gaseous products are formed from solid bodies, great heat being at the same time evolved, as in the explosion of nitre with charcoal, &c.

Neither can the heat of combustion be generally attributed to diminution of specific heat in the resulting compound; for in most cases the atoms of simple substances retain their original specific heat when they enter into combination (see ATOMIC WEIGHTS, i. 472, and HEAT). In other cases, on the contrary, combination is attended with an actual increase of specific heat, so that the result would be a production of cold, if heat were not developed from some other cause.

Thus, 1 lb. of hydrogen gas, of specific heat 3·293, combines, under the most violent evolution of heat, with 8 lbs. of oxygen of specific heat 0·236, producing 9 lbs. of water of specific heat 1·000, whereas calculation gives $\left(\frac{3·293 + 8 \,.\, 0·236}{9}\right) = 0·576$ as the mean of the two specific heats. If then water had a specific heat = 0·576, the quantity of sensible heat in the hydrogen and oxygen gases together would be exactly sufficient to bring the water formed to the same temperature as that of the gases themselves; but since the actual specific heat of water is 1·000, the quantity of sensible heat in the gases is not sufficient for this purpose; and if heat were not developed from some other cause during the combination of oxygen and hydrogen, the water produced would be much colder than the two gases before combination.

Berzelius, on reviewing these circumstances, justly concluded that all such explanations of the origin of fire are defective. He supposed that, in every chemical combination, there is a neutralisation of opposite electricities, and that this neutralisation produces the flame or fire, in the same way as it produces fire in the discharges of the Leyden phial and the voltaic battery, and in thunder. He admitted, however, that this hypothesis does not afford a satisfactory explanation of the union of the atoms after the discharge has taken place. (See CHEMICAL AFFINITY, i. 865.)

A more satisfactory explanation is that advanced by Sir Humphry Davy, viz. that the immediate cause of the phenomena of heat is motion, and that the laws of its communication are precisely the same as the laws of the communication of motion; that in fact, these phenomena are analogous to those of light, as expounded by the undulatory theory. On this principle we may explain the great heat produced by friction, and in explosions, such as those of oxide of chlorine, and chloride of nitrogen, cases in which heat and light are copiously displayed, at the same time that great enlargement of volume takes place, rendering the idea of the extrusion of a calorific fluid altogether inadmissible. Whenever the chemical forces which determine either composition or decomposition are energetically exercised, the phenomena of combustion, which are incandescence with a change of properties, are exhibited. In all cases, the heat and light depend on the same cause, and merely indicate the energy and rapidity of the reciprocal chemical attractions. No peculiar substance or phlogistic essence is necessary to the production of fire; but it is a general result of the actions of any bodies possessed of energetic chemical attractions or different electrical relations; and it is produced in all cases in which an intense and violent motion may be conceived to be communicated to the particles of bodies.

We now proceed to consider the circumstances which favour or retard combustion and determine the nature of flame, confining our attention chiefly to cases of combustion in the air. For the greater part of our knowledge on this subject we are indebted to the admirable researches of Sir Humphry Davy (Phil. Trans. 1817, pp. 45 and 77), which led him to the invention of the Miner's Safety-lamp. The subject may be treated under the following heads:—

1. The temperature and other conditions required to inflame different bodies.
2. The nature of flame and the relation between the light and heat which compose it.
3. The causes which modify and extinguish combustion.

The quantities of heat evolved in the combustion of different bodies will be more conveniently considered in the article HEAT (*q. v.*)

I. *Conditions of Inflammability.*

But few substances are capable of combining with *oxygen* at ordinary temperatures, and those which exhibit this capacity lose it at lower temperatures. The temperature required to bring about the combination of oxygen with any substance, the *burning point*, as it may be called, is different, not only for different substances, but even for the same substance, according as the combustion is to take place rapidly or slowly. Thus, phosphorus combines slowly with oxygen, or exhibits *slow combustion* at 25° C. (77° F.), but does not enter into rapid combustion till raised to 60° C. (140° F.) Charcoal likewise burns slowly below a red heat. Sulphur takes fire in the air at about 285° C. (550° F.) Most other elementary bodies require to be heated to redness before they take fire in the air or in oxygen gas. Several organo-metallic bodies, as zinc-methyl, cacodyl, and some of the antimonides of ethyl and methyl, take fire immediately on exposure to the air. Nitrogen cannot be made to unite with oxygen by elevation of temperature, except under peculiar circumstances; chlorine, bromine, and iodine not at all by heat, only by substitution.

Chlorine unites rapidly with hydrogen at ordinary temperatures, and under the influence of direct sunshine, produces a violent explosion. Many metals also burn when introduced into chlorine at ordinary temperatures. *Bromine* and *iodine* unite rapidly with phosphorus and with several metals, especially if in the finely divided state, at ordinary temperatures; but in a tube cooled with ice, phosphorus and iodine may be brought together without acting on each other.

Sulphur unites with many metals at a red heat, the combination being attended with vivid incandescence, *e.g.* with iron and copper.

The relative inflammability of different bodies in common air may be approximately estimated by fusing a series of globules of different sizes at the ends of thin iron wires, and lighting a number of very small flames of different substances, but all of the same size. A globule $\frac{1}{30}$ of an inch in diameter brought near an oil flame $\frac{1}{30}$ of an inch in diameter will, if cold, extinguish it at the distance of a diameter. The size of the globule required to extinguish the flame will afford a rough measure of the relative inflammability of the burning body. The combustibility of different gases may also be approximately measured by the sizes of the masses of heated bodies required to set them on fire. An iron wire $\frac{1}{40}$ of an inch thick at a cherry-red heat will inflame hydrogen, but not olefiant gas, which, however, is kindled by a wire $\frac{1}{8}$ of an inch thick at the same degree of heat. A wire $\frac{1}{500}$ of an inch thick must be heated to whiteness to inflame hydrogen, but it will kindle phosphoretted hydrogen at a low red heat. Carbonic oxide takes fire in the air by contact with an iron wire at a dull red heat; but the fire-damp of mines is not kindled by a wire $\frac{1}{40}$ of an inch thick heated even to whiteness. (Davy.)

Compression of the air does not appear to facilitate combustion, unless it takes place rapidly, and is consequently attended with considerable evolution of heat. Thénard, however, found that wood does not take fire in oxygen gas under the ordinary pressure at temperatures below 350° C., but under a pressure of 2·6 met. combustion begins at 252°. On the other hand, phosphorus in oxygen gas or common air exhibits slow combustion at a temperature which is lower in proportion as the gas or air is more rarefied; and a mixture of oxygen and phosphoretted hydrogen, which, under the ordinary atmospheric pressure, requires a temperature of 116·7° C. to inflame it, does not take fire at 118° when the density is increased to fifteen times its former amount; but if the mixture, contained in an inclined glass tube standing over mercury, be rarefied by setting the tube upright, combustion takes place at 20°. Döbereiner likewise found (J. pr. Chem. i. 114) that a mixture of equal measures of oxygen, hydrogen, and nitrogen gases contained in a detonating tube was always exploded by the electric spark, if the tube were open at the bottom, or merely closed with water; but not always when the tube was closed by a cork,—the compression appearing to offer an obstacle to the continuation of the combustion.

The combination of oxygen with inflammable gases and vapours is greatly facilitated by contact with *platinum* and certain other metals, the effect depending partly on the power possessed by the metal of condensing the gases on its surface or within its pores, if it be in the spongy or finely divided state, partly on a polarised condition of the molecules (see CONTACT-ACTION). When a clean plate or wire of platinum is immersed in a mixture of oxygen (or common air) and a combustible gas, a slow combustion takes place at first, by which the temperature of the solid body is raised,—and consequently, the process of combustion is not only sustained but actually accelerated; and at length the temperature of the solid body may be so much raised as to give rise to rapid combustion. The larger the surface of the metal, the more powerful is its action.

It was observed by Sir H. Davy that a mixture of oxygen gas or common air with hydrogen, carbonic oxide, olefiant gas, cyanogen, or vapour of hydrocyanic acid, alcohol, ether, rock-oil, or oil of turpentine, is brought into a state of slow combustion by contact with thin platinum foil or a spiral of platinum wire heated to a temperature short of redness,—that the heat thus developed brings the platinum to a state of bright ignition,—and that, with certain gases, rapid combustion at length ensues. He likewise found, as had been previously observed by Grotthus, that the mixture of oxygen and hydrogen gases heated not quite to redness in a glass tube, passed in a few minutes into the state of combination and formed water, without sensible evolution of light and heat. Erman showed that the platinum wire requires a temperature of only 50° to 51° C. in order to induce the combination of oxygen and hydrogen. E. Davy found that platinum-black (platinum in a state of division still finer than that of spongy platinum), moistened with alcohol, became incandescent in the air and induced combustion of the alcohol. Finally, Döbereiner discovered that freshly ignited spongy platinum (as it remains after ignition of ammonio-chloride of platinum) excites, even in the cold, first the slow, and then, under favourable circumstances, the rapid combustion of a mixture of hydrogen gas with oxygen or atmospheric air. It appears from the experiments of Döbereiner, Pleischl, Dulong, and Thénard, that this property is possessed (though in a less degree, so that in most cases the temperature must be raised, though never to the burning point) by other solid substances, both metallic and non-metallic, *e.g.* palladium, rhodium, iridium, osmium, gold, silver, cobalt, nickel, charcoal, pumice-stone, porcelain, glass, rock crystal, and fluor-spar.

These effects may be shown in either of the following ways:

1. Spongy platinum fastened to the end of a wire is suspended within a glass flask, which is then exhausted of air and filled with the mixture of oxygen and the combustible gas.—2. The gaseous mixture is contained in a vessel standing over mercury,

and the spongy platinum fastened to a wire is pushed up into it: or a piece of it is simply passed up by itself through the mercury into the gas. The platinum is best prepared for this purpose by forming a mixture of moistened clay and ammonio-chloride of platinum, or of sal-ammoniac and spongy platinum, into balls, and heating them gently: the balls thus prepared may be used several times.—3. The mixture of oxygen or air with the combustible gas is directed on the spongy platinum contained in a glass dish or a funnel.—4. The spongy platinum is attached to a fine platinum wire (for this purpose the platinum wire may be wound into a spiral, or a loose net may be made of it; and upon this a portion of ammonio-chloride of platinum, made into a thick paste with a small quantity of water, may be fastened, and then ignited); a stream of the combustible gas is then to be directed upon it: the gas is thus brought in contact with the platinum after first mixing with the air.—5. Fine platinum wire is wound from three to eight times in a spiral form round a thin glass rod or an iron wire, the turns of the spiral being kept very close together: it is then removed, and inserted by its lower extremity into the end of a glass tube, from which the combustible gas issues into the air;—or the lower turns of the spiral are fixed round the wick of a lamp fed with a combustible and volatile liquid, such as alcohol, ether, or a volatile oil; or again, the end of the wire is inserted into the middle of the wick or into a capillary tube into which the liquid rises. This arrangement serves for the *lamp without flame* or *glow-lamp* (i. 74). It is usual to set fire to the vapour, and let it burn till the platinum wire becomes red-hot; then, when the flame is blown out, the wire continues to glow.—6. A triangle of fine platinum foil is cemented by one of its corners into a thin glass rod, which serves for a handle, and held over the aperture (in some cases after being heated) from which the combustible gas issues into the air,—or else over a volatile liquid, such as alcohol or ether. The greater the purity of the ammonio-chloride, the more efficient is the spongy platinum prepared from it. As with platinum, so also with the other metals above named.

Effect of mechanical division.—Many finely divided substances are capable of burning at comparatively low temperatures, as shown by the following experiments:—When oxide of nickel, cobalt, or iron is reduced by hydrogen gas at a temperature of about 360° C., or not quite amounting to redness, or when oxalate of iron is heated in close vessels not quite to redness, whereby the iron is reduced, the metallic powder thus obtained burns with a glimmering light on being exposed to the air at ordinary temperatures. If the heat during the reduction be raised to redness, or if the metal reduced at a heat below redness be afterwards ignited in hydrogen gas, it will no longer exhibit spontaneous combustibility, possibly, because the metal when thus strongly heated agglomerates in denser masses: but if a quantity of alumina or glucina be mixed with the metallic oxide,—by mixing the solution with that of the salt of alumina or glucina, and precipitating by an alkali,—the metal, when reduced by hydrogen, even at a red heat (provided the heat has not been very intense), takes fire on exposure to the air, as readily as that which has been reduced at a lower temperature,—possibly, because the interposition of the earths, which are not reduced by the hydrogen, prevents the particles of metal from welding together. Copper reduced by hydrogen gas at a very moderate heat was likewise observed on one occasion to become covered, on exposure, with a film of oxide, without however taking fire. Iron reduced by hydrogen gas absorbs several times its volume of carbonic acid gas; it thereby loses its inflammability, which, however, it recovers by being again heated in hydrogen gas. This property of spontaneous inflammability may be explained in two different ways: 1. The metal reduced by hydrogen retains a portion of this gas enclosed among its particles; when exposed to the air, it induces combination between this substance and the oxygen of the air (after the manner of Döbereiner's process), and the great heat evolved in this combination causes the metal to take fire. Against this, however, it may be alleged that iron reduced from the oxalate cannot contain hydrogen gas enclosed amongst its particles (it may, however, contain carbonic oxide); and even when the metal is thrown into water, and the water driven off by evaporation, spontaneous combustion is still produced by contact of air.—2. The metal when exposed to the air absorbs the air mechanically, just as any porous body would do (and possibly it may absorb oxygen with peculiar avidity); and the heat developed by this mechanical absorption gives rise to the combustion. If the metal has been previously saturated with carbonic acid gas, of which perhaps it absorbs a larger quantity than of oxygen, it does not become heated by contact with the air (Magnus). Wöhler likewise found that intimate mixtures of charcoal and reduced metals often possess the property of taking fire at a red heat.

The spontaneous combustion of other porous substances, such as charcoal-powder or small coal, and especially of masses of tow, cotton, or rags saturated with oil, takes place in a similar manner. The substance absorbs and condenses the air within its pores; oxidation then commences immediately and raises the temperature, which again accelerates the oxidation; and thus the process goes on with continually increasing rapidity, till at length the mass bursts into flame. The low conducting power of such a porous mass greatly facilitates the combustion, by preventing the dissipation of the heat generated. Instances are known of olive oil igniting upon sawdust; of greasy rags from butter, heaped together, taking fire within a period of twenty-four hours; of the spontaneous combustion of tape-measures, which are covered with an oil-varnish, when heaped together; and even of an oil-skin umbrella put away in a damp state. The presence of moisture greatly promotes the spontaneous ignition of porous materials, such as hay or coal-dust, the water probably supplying oxygen to the combustible matter. (See Graham's *Report on the cause of the fire in the "Amazon."* Chem. Soc. Qu. J. v. 34.)

II. *Nature of Flame.*

The fire which accompanies the process of combustion appears either as *Glow* or *Incandescence*, when the burning body does not become gaseous before combustion, or as *Flame*, when the burning body is previously converted into gas or vapour. In the former case, the heat evolved at the surface of contact of the oxygen and the combustible body, charcoal or iron for example, heats the body and causes it to glow with various degrees of brightness, according to the temperature. Feebly glowing coals emit a dull red light (*cherry-red heat* or *dull red heat*); when more strongly heated, they emit a yellowish-red light (*bright* or *full red heat*): at still higher temperatures, a yellow light (*dull* or *commencing white heat*); then a yellowish, then a greenish, and lastly a bluish-white, intensely dazzling light (*bright*, *full*, or *dazzling white heat*).

When the combustible body is in the gaseous form, either originally or in consequence of the heat required to set it on fire, the mixture of this gas with the oxygen and the products of the combustion constitutes flame, which is, in fact, gaseous matter heated to incandescence. If the combustible gas or vapour, and the oxygen or air are uniformly mixed before ignition, the combustion takes the form of an explosion, combination taking place at once throughout the whole mass of gaseous matter, which consequently appears equally luminous throughout. A similar effect takes place when a combustible substance, such as sulphur or charcoal, is intimately mixed with a nitrate, chlorate, or other solid substance which readily gives up oxygen: if the temperature of such a mixture be raised to the burning point at one spot by friction, percussion, or the contact of a hot body, the ignition of the first few particles raises the temperature of the next, and then the action is propagated in an inappreciably short space of time throughout the whole mass, producing a sudden and violent evolution of gas, occupying many thousand times the volume of the original solid mixture. The noise attending the explosion arises from the violent concussion of the surrounding air produced by the sudden expansion of the burning gases.

But when the combustible gas or vapour issues from an orifice or a wick into the air, or into an atmosphere of oxygen, the combustion takes place gradually at the surface of contact of the two gases, and a flame is produced, consisting of an inner dark and less heated space filled with the combustible gas, and a glowing envelope marking the boundary at which the combustible gas and the oxygen come in contact and unite. That such is really the structure of flame may be shown by placing a piece of phosphorus on the wick of a burning spirit lamp, the phosphorus not taking fire till it is pushed outwards. If a piece of phosphorus be placed on a wooden support in the middle of a basin filled with alcohol, and the alcohol be set on fire, the phosphorus melts, but does not take fire till the alcohol is burnt away or extinguished, or till the flame is blown on one side, or air directed upon the phosphorus by means of the blowpipe. In a similar manner, a lighted candle will go out when placed in the midst of an alcohol flame.

The *brightness* or *illuminating power of flame* depends, not only on the degree of heat, but likewise on the presence or absence of solid particles which may act as radiant points. A flame containing no such particles emits but a feeble light, even if its temperature is the highest possible—the flame of hydrogen gas, for example. But in flames which do contain solid particles, the brightness increases with the temperature to which these particles are raised. Solid particles in a flame sometimes arise from the combination of the combustible body with oxygen, *e. g.* phosphoric acid or oxide of zinc in the combustion of phosphorus or zinc; sometimes, when the burning body is an organic hydrocarbon in the gaseous state, they consist of particles of carbon in the form of soot, separated in the interior of the flame by the heat of the burning envelope. A dull flame becomes brighter by the introduction of a solid body in a finely divided state.

The following substances give a *dull flame:* hydrogen gas, carbonic oxide gas, sulphur, selenium, arsenic, alcohol—and likewise coal-gas when it is mixed with a sufficient quantity of air to cause it to burn without deposition of soot: phosphorus also burns with a dull flame in chlorine gas, because the chloride of phosphorus, which is the product of the combustion, remains in the gaseous state (H. Davy). When a spiral of platinum wire or a piece of asbestos is held in either of these flames, or some powdered oxide of zinc thrown into it, the solid matter immediately becomes white, and emits a vivid light (H. Davy). Paper soaked in solution of chloride of calcium and burnt in the flame of a spirit lamp, leaves a white network of ashes, which, when held in the feeblest alcohol flame, emits a brilliant light. (Talbot, Phil. Mag. [3] iii. 114.)

If alcohol vapour be projected from one set of tubes, and oxygen gas from another set, upon a ball of quicklime, having a stem by which it is fastened to a wire, the alcohol burning in the oxygen gas heats the ball to the most dazzling whiteness; so that the light, when reflected by a concave mirror placed behind it, is plainly visible at the distance of 68 miles. Zirconia gives a light somewhat less powerful than that of lime; that produced by magnesia is only half as strong. (Drummond, Ed. J. of Sc. 5, 319.) By the oxy-hydrogen blowpipe (i. 613) lime is rendered much more brightly luminous than by alcohol and oxygen gas. Supposing the intensity of light of a wax candle = 1, that emitted by a cylinder of lime whose circumference is one-fifth of that of the flame of the candle, is equal to 153 when it is ignited by the oxy-hydrogen flame; to 76, in the flame of ether and oxygen; to 69, in that of alcohol and oxygen; and to 19, in that of coal-gas and oxygen. Unburnt chalk, white clay, and magnesia, give much less light than burnt chalk.

A *bright flame* is produced by the following bodies:—

1. Those which in combination with oxygen form a solid compound: phosphorus, potassium, antimony, bismuth, zinc, and most other metals. (Davy.)

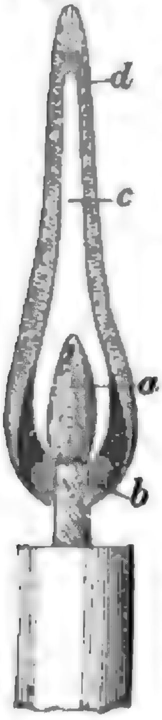
2. Compounds containing carbon, from which a portion of the carbon is separated in the form of soot, by the heat produced at the part where the combustion actually takes place, the separated carbon being first brought to a state of vivid incandescence, and subsequently burnt when it comes in contact with oxygen. This is the case with marsh-gas, olefiant gas, ether, volatile oils, fats, resins, &c. (H. Davy). The flame of alcohol may likewise be rendered bright by the presence of any substance which causes the carbon to separate from it. Thus, chlorine gas mixed with the flame of alcohol increases its luminosity, because, by combining with the hydrogen, it causes a deposition of solid carbon. Vapour of dioxide of osmium likewise gives luminosity to the flame of alcohol, by giving up osmium and separating carbon from the alcohol. To produce this effect, a piece of osmium is laid on the edge of a piece of platinum-foil, and the foil held over the alcohol flame, so that the osmium may burn, and the vapours of the oxide may mix with the vapour of alcohol (Berzelius). The flame of hydrogen or marsh-gas may be rendered bright by passing the gas through coal-tar naphtha, rock-oil, or some other volatile hydrocarbon, the vapour of which then mixes with the gas and brightens the flame by the separation of its carbon.

On the contrary, by mixing a jet of carbonaceous gas or vapour with oxygen, as in Bunsen's gas-burner, in which air is admitted just above the point where the stream of gas enters the burner, so that the gas and air become well mixed before they reach the orifice, a complete combustion of the carbon is obtained, and only gaseous products are formed, the result being a very hot smokeless flame of feeble luminosity. A similar flame is obtained by laying a sheet of wire-gauze on the top of the chimney of an Argand gas-burner, and setting fire to the gas above the gauze. The gas then becomes well mixed with air in passing up the chimney, and the carbon is completely burned as before.

The more slowly a carbonaceous substance is burned, the greater is the quantity of carbon separated from it; the brightness of the flame is, however, diminished in the same proportion, because the particles of carbon are less strongly heated. On the contrary, the quicker the combustion, the smaller is the quantity of carbon separated; but the temperature to which it is raised is so much the higher, and consequently it emits a brighter light.

The flame of highly carbonised substances, such as a wax or tallow candle, consists of four parts, as represented in fig. 129. *a*, a *dark inner cone*, surrounding the wick, and consisting of the combustible gas and vapour issuing therefrom, mixed with atmospheric nitrogen and the products of combustion, viz. water and the oxides of carbon; *b*, a *light blue zone* at the bottom of the flame, and reaching a little way up the inner cone. In this part, the combustible matter of the inner cone comes in contact with the oxygen of the air not yet rarefied by the heat, and is completely burned just as in the inner blowpipe-flame (i. 613), producing a light of the same bright blue colour. *c*, a *highly luminous cone* surrounding the dark inner cone. In this part, the supply of oxygen is not sufficient, excepting at the outer surface, for the complete combustion of the carbon, which is therefore separated in minute solid particles, and these being strongly heated by the combustion, become highly incandescent: if a cold body be introduced into the flame, these particles of carbon are deposited as soot. *d*, the *mantle*, a feebly luminous, yellowish cone surrounding the entire flame, excepting just at the bottom, and consisting of atmospheric air heated to incandescence, and mixed with the final products of the combustion. This part of the flame is often confounded with the blue zone, from which, however, it is really distinct. The best mode of observing it is to cut out a piece of cardboard of nearly the shape of the flame, and hold it at such a distance from the eye as just to hide the luminous cone.

Fig. 129.



The flame of an Argand lamp, which is supplied with air within as well as without, may be compared to the flame of an ordinary lamp or candle flattened out, and then bent into a cylinder. It contains the same parts as the conical flame, but from the form of the wick, the dark zone is necessarily very thin.

The composition of the flame of wax and tallow burning from a wick has been accurately investigated by Hilgard (Ann. Ch. Pharm. xcii. 129; Jahresb. f. Chem. 1854, p. 287). The lamp used in the experiments consisted of a shallow cylinder containing the fuel, and having in its axis a glass tube, over the upper end of which the cylindrical wick was drawn. Through this tube, which was capable of sliding up and down, a narrower tube connected at its lower end with an aspirator passed upwards into the flame. This narrow tube was attached to the outer tube by means of a caoutchouc connecter, in such a manner that no air could pass through the wide tube into the flame. By this arrangement, the gases could be collected at any required height in the flame; they then passed through a series of condensers, and finally into a glass tube in which they were sealed up for examination.

In the following table, the composition of the gases at different heights (in millimetres) above (+) and below (−) the edge of the wick is given in percentages by volume; the symbol C^2H^4 includes ethylene and the hydrocarbons polymeric with it. X denotes the weight of liquid and solid matter condensed from a litre of the flame-gas.

Composition of Wax and Tallow flames.

Beef-tallow Flame.								Wax Flame.							
Height.	X.	N.	CO^2.	CO.	C^2H^4	CH^4.	H.	Height.	X.	N.	CO^2.	CO.	C^2H^4.	CH^4.	H.
+9	0·12	75·92	14·46	5·66	1·82	1·15	1·30	+10	0·12	76·62	11·70	5·16	3·70	0·85	1·97
								8	0·15	73·96	11·46	5·73	5·16	0·88	2·41
6	0·11	72·28	10·90	6·25	6·04	2·68	1·85	6	0·18	70·34	10·53	5·80	9·21	1·70	2·71
4	0·13	64·40	10·24	6·68	13·10	2·70	2·88	4	0·32	64·15	9·99	5·86	14·29	2·93	2·78
2	0·38	59·01	10·14	7·[illegible]	17·12	3·78	2·73	2	0·48	64·09	10·07	5·62	14·89	2·62	2·73
0	0·70	63·57	7·13	4·60	18·77	5·20	0·73	0	1·00	65·36	10·00	5·42	14·23	2·31	2·69
−3	1·49	61·72	11·73	6·27	15·13	4·00	0·15	− 3	1·57	63·61	10·78	5·70	14·29	3·08	2·64
Without the Nitrogen:—															
+9	. .	. .	60·06	23·46	6·29	4·79	5·40	+10	. .	. .	50·01	22·08	15·83	3·64	8·43
								8	. .	. .	44·00	19·80	19·80	3·28	10·81
6	. .	. .	39·31	22·54	21·79	9·68	6·68	6	. .	. .	35·57	30·98	30·98	5·75	9·16
4	. .	. .	28·78	18·75	36·81	8·08	7·58	4	. .	. .	27·87	39·87	39·87	8·18	7·75
2	. .	. .	24·73	17·62	41·78	9·21	6·66	2	. .	. .	28·04	41·43	41·43	7·29	7·60
0	. .	. .	19·58	12·68	51·51	14·29	2·00	0	. .	. .	28·86	41·07	41·07	6·67	7·75
−3	. .	. .	30·65	16·38	39·55	10·44	3·07	− 3	. .	. .	29·62	39·27	39·27	5·48	6·97

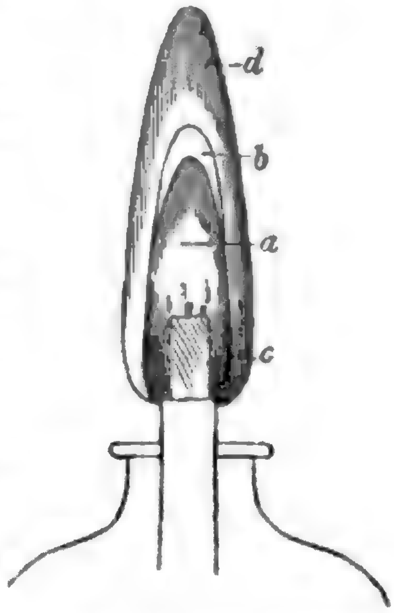
The large quantity of nitrogen in the interior of the flame arose from the circumstance, that the air entered the flame in a nearly horizontal direction, especially at the lower part. The proportion of nitrogen is a minimum at 2mm. above the edge of the wick, chiefly because the greater heat and increasing amount of decomposition in this part of the flame produce a larger amount of permanent gases. The quantity of carbonic anhydride is nearly inversely proportional to that of the hydrocarbons, C^nH^{2n}. When the nitrogen is deducted, the sums of the amounts of carbonic anhydride, ethylene, &c., and carbonic oxide are nearly constant. The total quantity of these three gases appears to alter but slightly from the bottom of the flame to a height of 7mm. or 8mm; at a greater height, it appears to increase, in consequence of the excess of the products of oxidation.

The inner cone of the flame contains the unburnt gases issuing from the wick, mixed with atmospheric nitrogen and carbonic oxide, carbonic acid, and water, produced by the combustion going on in the outer cone, but *no free oxygen*, that gas being completely converted into the products just mentioned in passing through the outer cone. The composition of the gases at different heights of the flame is determined by the natural action of the combustible gases in the inner cone and the oxidised products proceeding from the outer part.

The luminous envelope surrounding the inner cone varies in composition from without inwards, the outer portion containing a considerable quantity of free oxygen which gradually diminishes as it penetrates inwards. The thickness of the luminous envelope increases towards the upper part of the flame, because this portion contains the oxidised products ascending from below, in addition to those directly formed there, so that the proportion of combustible gases in the upper part of the flame is less, the combustion is slower, and the oxygen of the air can penetrate to a greater depth; hence the luminous envelope diminishes in brightness and increases in thickness from below upwards, and near the apex it presents the appearance of a solid cone. The reducing part of the flame is at the surface of contact of the inner cone and the luminous envelope.

The flames of combustible bodies which do not undergo the decompositions above described, differ considerably in composition from those of wax or tallow. The luminous cone is often absent, more rarely the mantle: the inner cone is of course always present, and the blue zone is almost always represented by the part where the still undiluted combustible gas comes in contact, at a comparatively low temperature, with air containing its full amount of oxygen. The flame of **carbonic oxide** exhibits a distinct dark cone (consisting of unburnt gas), a dark blue zone, and a yellowish-red mantle not sharply defined from the surrounding air. The flame of **sulphur** has a blue zone at the bottom and a violet-reddish mantle, the colour with which sulphur-vapour burns when previously strongly heated. In the **alcohol-flame** (*fig.* 130) the inner cone *a* is very large, in consequence of the volatility of the combustible substance: the luminous cone *b* is small, because there is but little carbon separated; and the mantle *d* appears very much developed, because the eye is not dazzled by a bright luminous cone.

Fig. 130.



The composition of the flame of ***coal-gas*** has been examined by **Landolt** (Pogg. Ann. xcix. 389), by a method similar to that above described for the wax and tallow flames. The gas, properly purified from carbonic acid, oxygen, and aqueous vapour, was passed, under pressure of a column of water, 17 Paris lines high, into a brass box, having at the top a circular aperture 7mm. wide, and a tube of nearly the same diameter passing tightly through the bottom, and terminating on a level with the circular opening, so that the gas was made to issue through the narrow ring-shaped slit thus formed. A tube connected with an aspirator passed up through the brass tube into the flame, as in Hilgard's experiments. The flame was protected from draughts of air by a glass cylinder suspended over it and reaching to within 20mm. of the burner; it was from 95 to 100mm. high when burning freely, and from 85 to 95mm. while gas was being drawn out of it. The following table gives the composition of the purified coal-gas (L) introduced into the burner, and that of the flame-gas, at various heights, D mm., above the ring-shaped aperture, in percentages by volume (F).

Composition of Coal-gas flame.

D . . .	0mm.		10mm.		20mm.		30mm.		40mm.		50mm.	
	L	F	L	F	L	F	L	F	L	F	L	F
Hydrogen .	39·30	20·34	41·04	12·45	44·00	9·23	44·00	4·99	41·37	3·43	41·37	2·50
Marsh-gas .	40·56	30·31	40·71	25·14	38·40	11·52	38·40	6·92	38·30	2·82	38·30	0·79
Carbonic oxide	4·95	6·59	7·64	11·71	5·73	5·71	5·73	4·68	5·56	5·26	5·56	5·45
Ethylene . .	4·04	3·80	5·10	3·59	4·13	1·86	4·13	1·65	5·00	0·90	5·00	0·60
Tetrylene .	3·15	2·75	2·18	2·65	3·14	1·34	3·14	1·00	4·34	0·77	4·34	0·58
Oxygen . .	—	0·59	—	0·65	—	0·19	—	—	—	—		—
Nitrogen . .	8·00	26·40	2·75	32·20	4·23	57·25	4·23	59·18	5·43	64·01	5·43	66·50
Carbonic acid .	—	1·74	0·58	1·95	0·37	4·11	0·37	4·81	—	5·62	—	7·01
Water . .	—	7·48	—	9·66	—	15·79	—	16·87	—	17·19	—	16·39

From these results, Landolt has calculated the proportions of coal-gas and air which by their mutual action form the several parts of the flame-gas. The results are somewhat discordant, according as the carbon, hydrogen, or nitrogen is taken as the basis of the calculation; but the most probable results are given in the following table, in which A denotes the volumes of atmospheric air which have mixed with 100 vols. coal-gas to produce the flame-gas at the several heights, D, indicated in the first line. 100 + A = M volumes of this unburnt gaseous mixture yield, after combustion, V volumes of flame-gas. The composition of the M volumes of unburnt gaseous mixture and of the V volumes of flame-gas produced by their combustion are given in the lower part of the table.

Composition of Coal-gas flame.

D . . .	0mm.		10mm.		20mm.		30mm.		40mm.		50mm.	
A . . .	27·08		45·43		172·76		227·73		335·30		381·66	
M . . .	127·08		145·43		272·76		327·73		435·30		481·66	
V . . .	111·41		120·09		245·96		311·37		422·59		461·23	
	M	V	M	V	M	V.	M	V	M	V	M	V
Hydrogen . .	39·30	22·66	41·08	14·95	44·00	5·49	44·00	15·54	41·37	14·80	41·37	11·95
Marsh-gas . .	40·56	33·77	40·71	30·20	38·40	28·34	38·40	21·55	38·80	11·92	38·30	3·64
Carbonic oxide .	4·95	7·34	7·64	14·07	5·73	14·05	5·73	14·58	5·56	22·24	5·56	25·14
Ethylene . .	4·04	4·23	5·10	4·31	4·13	4·58	4·13	4·83	5·00	3·80	5·00	2·77
Tetrylene . .	3·15	3·06	2·18	3·18	3·14	3·29	3·14	3·11	4·34	3·25	4·34	2·68
Oxygen . .	5·67	0·65	9·52	0·78	36·21	0·47	47·73	—	70·28	—	79·59	—
Nitrogen . .	29·41	29·41	38·66	38·66	140·78	140·78	184·23	184·23	270·45	270·45	307·16	307·16
Carbonic acid .	—	1·94	—	2·34	0·37	10·11	0·37	14·98	—	23·76	—	32·34
Water . .	—	8·34	—	11·60	—	38·85	—	52·55	—	72·67	—	75·61
	127·08	111·41	145·43	120·09	272·76	245·96	327·73	311·37	435·30	422·59	481·66	461·23

The sudden increase in the quantity of air mixing with the combustible gas between the heights of 10 and 20mm., is attributed by Landolt to the effect of the glass cylinder. The proportion of carbonic acid does not increase towards the upper part of the flame so rapidly as might be expected, probably on account of the reduction of that gas to carbonic oxide by the the ignited carbon in the flame; hence also the sudden increase in the proportion of carbonic oxide between the heights of 30 and 40mm. The quantities of the several combustible gases in the flame diminish from below upwards, at rates proportional to their combustibility. From 0 to 20mm. the decrease of the hydrogen is the most rapid; the increase in the proportion of this gas in the flame above the height of 20mm. is probably due to the reducing action of the ignited carbon in the aqueous vapour. The marsh-gas diminishes more slowly, and the heavy hydrocarbons still more slowly, the latter indeed remaining nearly unaltered in the flame up to 40mm., and burning only in the higher part.

The *brightest light* was found to be given out by the part of the flame a little above the top of the dark cone. In a gas-flame 100mm. high, in which the dark cone reached to about 65mm., the highest part was at 70mm., and supposing the brightness of this part = 100, that of the other parts of the flame was found to be as follows:

	mm.	mm.	mm.	mm.	mm.	mm.
Height above burner . .	80	70	60	50	40	30
Brightness at the edge . .	66	100	77	47	20	4
Brightness in the middle .	66	100	59	24	5	—

The *size of a flame* is greater in proportion as a larger quantity of oxygen is required to consume a given volume of the rising combustible gas, and also as the surrounding oxygen is mixed or combined to a greater extent with foreign gases; for, in that case, the combustible gas must present a larger circumference, and a greater number of points of contact to the oxygen, in order that the latter may be consumed as fast as it is supplied.

When different combustible gases are made to flow from a jet, in streams of given strength, into oxygen gas and mixtures containing it, the following effects are observed: Hydrogen gas gives a much smaller flame than olefiant gas (1 volume of hydrogen requires half a volume of oxygen, and 1 volume of olefiant gas requires 3 volumes of oxygen to burn it). Hydrogen gas mixed with nitrogen gives a still smaller flame than pure hydrogen. The flame of hydrogen gas in oxygen is smaller than that of the same gas in air; but there is this anomaly observed, that hydrogen gives a smaller flame in air than it does in chlorine or nitrous oxide gas,—although one volume of hydrogen gas requires 2·4 volumes of air and only 1 volume of chlorine or of nitrous oxide gas. This peculiarity is probably due to the different degrees of diffusibility of the gases through each other.

The *colour of the flame* depends partly on its temperature, partly on the nature of the substances contained in it.

Cold carbonic oxide gas gives a blue flame in burning; but if it has previously been heated, it gives a yellowish red flame. Hydrogen and other gases, which in burning evolve more heat than is evolved by carbonic oxide, exhibit a yellowish red flame even when set on fire in the cold. But when hydrogen gas issues from a fine jet (as in Marsh's apparatus) against a porcelain slab held close in front of it, a pale green flame is produced,—possibly in consequence of the cooling action of the porcelain. The blue flame at the lower part of the flame of a candle likewise indicates a comparatively low temperature. It is remarkable that in the glowing combustion of solid bodies the colours exhibit exactly the opposite relation (p. 1094).

The addition of boric acid, or of a metallic chloride and oil of vitriol, to alcohol, gives the flame a green colour—or, when it is more strongly heated, it turns yellow. Chloride of strontium or chloride of calcium colours the flame of alcohol red; chloride of barium, or common salt, colours it yellow; protochloride of copper gives it a bright red colour, with green and blue edges. Copper covered with oxide or sulphide (but not clean copper), held in the flame of alcohol, colours it green. The flames of other burning bodies undergo similar alterations. Chloride of strontium reddens the flame of hydrogen, marsh-gas, and olefiant gas, as also that of a candle—but only so long as the salt itself remains moist; on the flame of sulphur it has no effect. In all these cases, a portion of the added substance undoubtedly volatilises: but whether it volatilises undecomposed, so that the colour of the flame is altered merely by the presence of boracic acid, chloride of strontium, chloride of copper, &c., or whether decomposition takes place, so that boron, strontium, calcium, barium, or copper is introduced into the flame in the reduced state, is there burnt, and thereby produces a different colour—is a question not yet decided. Davy suggested the latter explanation.

Respecting the prismatic spectra produced by flames in which various salts, &c. are ignited, see ANALYSIS (i. 214), also LIGHT.

In ordinary flames, the combustible gas occupies the interior, and is surrounded by atmospheric air or oxygen gas. But the combustion may likewise be sustained by directing a stream of oxygen gas, air, &c., into a vessel filled with the combustible gas. The interior dark part of the flame then consists of oxygen gas; and this gas seems, as it were, to burn in the combustible gas. In this manner, oxygen gas (and also chlorine) may be made to burn in hydrogen; likewise oxygen gas, common air, vapour of pernitric oxide (or chlorine gas, with large deposition of soot) in olefiant gas. To produce this effect, a stoppered bell-jar standing over water is filled with olefiant gas, the stopper removed, the gas set on fire, and the oxygen tube, which is fitted into a cork, plunged into the olefiant gas, the cork serving to close the aperture. Or a quantity of chlorate of potassium, contained in a small basin suspended from the cork, may be heated till it evolves oxygen gas, and then plunged into the olefiant gas previously set on fire at the mouth of the jar: the combustion then goes on, producing a beautiful light, the colour of which may be variously modified by the addition of nitrate of sodium, strontium, or copper (Kemp, J. Pharm. xx. 413; also J. pr. Chem. iii. 44).

The flame of oxygen in hydrogen gas is green, even when both gases are quite pure: that of oxygen in marsh-gas is yellow. The first-mentioned flame is much larger than the other, because a measure of oxygen gas requires two measures of hydrogen, and only half a measure of marsh-gas (Hess, Pogg. Ann. xliv. 336; also J. pr. Chem. xiii. 516).

The flame is smaller when oxygen or nitrous oxide gas, or vapour of pernitric oxide, or chlorine gas is made to pass into hydrogen gas, than in the contrary case; according to what was said on p. 1098, the contrary might have been expected. A much smaller flame is produced when oxygen passes into olefiant gas than when it passes into hydrogen. With olefiant gas, the flame is dark within; then follows a brilliant envelope, hot enough to melt platinum; then, towards the outside, a dark yellow flame, lengthening above and containing soot, the greater part of which remains unburnt. When oxygen gas is blown into boiling sulphur, a yellow flame is produced, dark within, red on the outside and at the apex: air gives a smaller flame than oxygen, dark within, blue without, and red at the apex (Waldie, Phil. Mag. [3] xiii. 86).

The *Blow-pipe flame* is of the same character as those just mentioned, inasmuch as the air is blown into the middle of the ascending combustible vapour. The strongest heat exists at that part of the flame where the dark cone of injected air terminates in a bluish vertex, and the burning envelope which surrounds it concentrates itself upon a single point (i. 611).

III. *Causes which modify and extinguish Combustion.*

When the slow or rapid combination of a body with oxygen has once been set up by elevation of temperature, the continuance of this combination, after the supply of heat from without has been withdrawn, depends in general on the following condition: — Whether the quantity of heat, which the body in combining with oxygen evolves in a given time, is equal to that which, in the same time, is carried away by surrounding bodies; and consequently, whether the body remains at the temperature necessary for combustion; — and in particular: 1. On the difference between the temperature at which the body will combine with oxygen, rapidly or slowly, and the external temperature; 2. On the quantity of heat which it evolves in burning; 3. On the rarefaction or condensation of the oxygen gas; 4. On the greater or smaller admixture of foreign gaseous bodies not contributing towards the combustion; 5. On the presence of liquid or solid heat-conducting bodies.

1. Iron and diamond require a white heat to make them burn rapidly: hence, when they are heated in the air till they begin to burn, the combustion ceases as soon as the access of heat from without is discontinued, whereas sulphur, and other easily inflammable bodies, continue to burn.

2. Carbonic oxide gas, which is as easily inflammable as hydrogen, does not exhibit rapid combustion after it has been rarefied to about one-fourth of its ordinary density, because it evolves less heat during combustion. (H. Davy.)

3. A certain degree of rarefaction prevents the continuance of combustion; because combination, and therefore, also, development of heat, is retarded by it. Detonating gas (a mixture of two measures of hydrogen gas and one of oxygen), when rarefied to $\frac{1}{18}$ of its ordinary density, no longer explodes by the electric spark (H. Davy). Hydrogen gas, mixed with air in the right proportion, will not take fire under an external pressure of five inches (Grotthuss). Hydrogen gas issuing from a jet into the air exhibits rapid combustion under a fourfold rarefaction of the air, burning even with a larger flame than before, but is extinguished when the density is reduced to between $\frac{1}{5}$ and $\frac{1}{6}$ of its ordinary amount.

The burning vapour of alcohol, ether, or wax, is extinguished, under these circumstances, by a five or sixfold rarefaction; sulphuretted hydrogen by a sevenfold rarefaction of the air. Sulphur continues to exhibit rapid combustion, even when the air is rarefied fifteen times; phosphorus, when the density is reduced to $\frac{1}{60}$; while the easily inflammable variety of phosphoretted hydrogen gas produces a flashing light, even in the best vacuum that can be made with the air-pump. Vapour of ether, in air rarefied thirty times, still produces a feeble flame on the introduction of a red-hot iron. Slow combustion on the surface of platinum is exhibited by marsh-gas, down to a fourfold rarefaction of the air; by carbonic oxide, to sixfold; by vapour of alcohol, ether, or wax, to eightfold; by olefiant gas, to ten or elevenfold; by hydrogen gas, to thirteenfold; and by vapour of sulphur, down to twentyfold rarefaction of the air. By elevation of temperature, the limits of inflammability are still further extended; so that detonating gas rarefied eighteen times, and heated to redness, exhibits a light as if from combustion, on the passage of an electric spark. (H. Davy.)

Within certain limits, however, the rate of combustion is independent of the density of the surrounding atmosphere. Frankland found that a stearin candle burned away at the same rate on the summit of Mont Blanc and in the valley of Chamounix. The brightness of the flame is, however, greatly diminished by rarefaction of the air. A coal-gas flame, burning in artificially rarefied atmospheres, exhibited an average decrease of illuminating power amounting to about 5·1 per cent. for each diminution of 1 inch of mercurial pressure. (Proc. Roy. Soc. xi. 137.) See FLAME.

4. Foreign gaseous bodies, which contribute nothing to combustion, absorb a portion of the heat generated by the combination, and reduce the temperature below the burning point, the rapidity of their action being proportional to their quantity, mobility, and capacity for heat. Not only do bodies in general burn more rapidly in oxygen gas than in atmospheric air, which contains only one volume of oxygen to four of nitrogen; but iron and diamond, which, when once set on fire, continue to burn in oxygen gas, are immediately extinguished in atmospheric air. In air four or five times compressed — which, therefore, contains one volume of oxygen gas — candles, hydrogen gas, sulphur, charcoal, and iron, do not, in consequence of the abstraction of heat by the nitrogen, burn more rapidly than they would in uncompressed air, to which $\frac{1}{5}$ of a volume of oxygen had been added. One volume of detonating gas loses its power of taking fire by the electric spark, if there be added to it $\frac{1}{2}$ a volume of olefiant gas, $\frac{2}{3}$ of a volume of fluoride of silicium, 1 volume of marsh-gas, 2 volumes of sulphydric or hydrochloric acid gas, 8 volumes of hydrogen in excess, 9 volumes of oxygen in excess, or 11 volumes of carbonic oxide: 5 measures of aqueous vapour do not destroy the inflammability of 1 measure of detonating gas (H. Davy). According to

Humboldt and **Gay-Lussac** (Gilb. Ann. xx. 49), the inflammability of one volume of detonating gas is destroyed by the admixture of 5 volumes of oxygen, or 4·7 volumes of hydrogen gas. Marsh-gas is no longer inflammable by the electric spark, when it is mixed with 11 measures of oxygen instead of the 2 measures which it actually requires to combine with it (**H. Davy**). Coal gas burns continuously in a mixture of 1 measure of oxygen and 7 of nitrogen, but is extinguished when the quantity of the latter amounts to 8 measures; it burns in a mixture of 1 measure of oxygen with 3, but not with 4 measures of hydrochloric acid gas; with 2⅓, but not with 3 measures of carbonic acid: with 2, but not with 2½ measures of fluoride of silicium. The greater the density of the inactive gas, the smaller is the quantity which suffices to stop the combustion; because the combustible gas diffuses itself more readily through a heavy than through a light gas, and therefore cools down the faster (**Waldie**). A lighted candle is extinguished in air to which ⅛ of its volume of hydrochloric acid gas, or $\frac{1}{16}$ of fluoride of silicium, has been added. When combustible bodies burn in a confined space, the relative quantity of nitrogen, &c. becomes increased, partly by consumption of oxygen, partly by formation of gaseous products of combustion, such as carbonic acid, sulphurous acid, &c.; and thus the combustion is brought to an end. In one and the same limited space, a candle goes out first, then hydrogen gas, then sulphur; while the slow combustion of phosphorus will go on as long as the smallest quantity of oxygen remains. (**H. Davy**.)

5. Solid burning bodies are extinguished when laid on good-conducting supports, *e. g.* glowing coals on considerable masses of metal.—A mixture of a combustible gas and oxygen will not take fire in very narrow tubes, because their sides cool down too quickly: this is the principle of the oxy-hydrogen blow-pipe (i. 616). From the same cause, the flame of a mixture of combustible gases and common air is often unable to pass through the meshes of wire-gauze: the passage of the flame takes place, however, with greater facility, the lower the temperature at which the gas takes fire, the greater the heat evolved by its combustion, the more quickly it is forced through the apertures by pressure or draught, the wider the meshes, the smaller the mass and specific heat of the metal of which the gauze is made, and the higher its temperature. Above a certain temperature, all flames pass through it. The flame of a cotton thread may be extinguished by holding over it, even at some distance, a ring of fine iron wire, or a thicker ring of glass (**Davy**). On this impenetrability of wire-gauze by the flame of light carburetted hydrogen gas in coal-mines, is based the *Safety-lamp* of Sir H. Davy, which consists essentially of a common oil-lamp having its flame surrounded by a cylinder of wire-gauze. When this lamp is taken to a part of the mine containing an explosive mixture of gas and air, the interior of the cylinder becomes filled with a blue flame; but this flame is not communicated to the explosive mixture outside, because it is cooled down below the burning temperature in its passage through the meshes of the gauze. (See the article SAFETY LAMP, in *Ure's Dictionary of Arts, Manufactures, and Mines*, iii. 612; also *Ronald's and Richardson's Chemical Technology*, i. [2] 511.)

The same principle is applied in many elegant contrivances now in use in chemical laboratories for burning a mixture of gas and air, so as to produce a hot smokeless flame (p. 1095), the mixture of gas and air being made to pass through a sheet of wire gauze, and set on fire at the other side, so that the flame cannot extend to the orifice whence the gas issues.

Motion of the air, produced by draught or by the bellows, accelerates combustion and increases the intensity of the heat, by continually bringing fresh portions of air in contact with the burning body. Very rapid motion of the air may however extinguish combustion, either by the cooling—if the quantity of air supplied in a given time is such that the burning body cannot in the same time consume the whole of its oxygen; or by blowing the burning vapour away from its source, so that the flame can no longer communicate with the fresh matter which issues.

Fire-extinguishing substances act either by cooling, as water does,—or by covering the burning body and thereby impeding the access of air—as when a rug or other not easily combustible body is thrown on a mass of light burning materials, or when a fire is choked with earth or ashes;—or lastly by surrounding the burning mass with an atmosphere not containing oxygen. This is the principle of *Phillips's Fire-annihilator*, in which a mixture of 20 pts. charcoal, 60 pts. saltpetre, and 5 pts. gypsum, is set on fire by means of chlorate of potash, sugar, and sulphuric acid, the heat produced by the combustion being made at the same time to convert into vapour a quantity of water contained in the apparatus. The result is the instantaneous production of a large quantity of steam, carbonic acid and other inactive gases, which can be at once directed on the burning mass. (See *Ure's Dictionary of Arts, Manufactures, and Mines*, ii. 212.)

With regard to the efficiency of steam in extinguishing fires, Mr. Graham observes in his "Report on the fire in the Amazon," already quoted (p. 1094), that "steam can only be said to be efficient in extinguishing flame, or a blaze from light objects, and is not to be relied on beyond an early stage of a fire. Upon a mass of red-hot cinders, the extinguishing effect of steam is insensible." The same is probably true with regard to carbonic acid, nitrogen, and other gases.

Method of diminishing the inflammability of light fabrics.—Much attention has lately been devoted to the problem of rendering muslin and other light fabrics non-inflammable, with the view of preventing the terrible accidents, which so frequently arise from ladies' dresses coming in contact with the flame of a candle or the fire in a grate. This object is attained by steeping the fabric in a saline solution, and then drying it in the ordinary way. The fibre is thereby surrounded with a crust of incombustible matter, which prevents it from taking fire by momentary contact with a burning body, and causes it, even if held in a flame, to burn with a slow smouldering combustion, without bursting into flame.

Almost any salt will produce this effect, but the greater number are unfit for application to articles of dress, because they injure the texture, rendering the fabric harsh, and destroying all its beauty. The salt which is found to answer most completely all the required conditions, is the *neutral tungstate of sodium.* Muslin steeped in a solution containing 20 per cent. of this salt is perfectly non-inflammable when dry, and the saline film left on its surface is smooth and of a fatty appearance like talc, and therefore does not interfere with the process of ironing, but allows the hot iron to pass smoothly over the surface. The non-fulfilment of this latter condition completely prevents the use of many other salts—such as sulphate and phosphate of ammonium, which are otherwise efficacious in destroying inflammability—for all fabrics which have to be washed and ironed.

The use of the tungstate of sodium for this purpose offers but one difficulty, viz. the formation of an acid tungstate of little solubility. This inconvenience may, however, be obviated by the addition of a small quantity of phosphoric acid or phosphate of sodium. The best way of preparing a solution of minimum strength for the purpose, is to dilute a concentrated solution of the neutral tungstate with water to 28° Twaddell, and then add 3 per cent. of phosphate of sodium. The solution is found to keep, and to answer its purpose well; it is now constantly used in Her Majesty's laundry (Versmann and Oppenheim, *Communication read before the British Association at Aberdeen*, 15th Sept. 1859; Pharm. J. Trans. [2] i. 385). The use of phosphate of ammonium for preserving light fabrics from ignition was proposed, many years ago, by Gay-Lussac.

COMENAMETHANE. Syn. with Comenamate of Ethyl.

COMENAMIC ACID, $C^6H^5NO^4 + 2H^2O = \left.\begin{matrix} N.H^2.(C^6H^2O^3)'' \\ H \end{matrix}\right\} O + 2H^2O$. (How, Ed. Phil. Trans. xx. [2] 225; Ann. Ch. Pharm. lxxx. 65.)—This acid is produced by the dehydration of acid comenate of ammonium, $C^6H^3(NH^4)O^5 - H^2O = C^6H^5NO^4$. It may be prepared by heating the salt to 199° C. in a sealed tube, and precipitating the aqueous extract with hydrochloric acid; or better, by boiling aqueous comenic acid with excess of ammonia till nearly all the ammonia is expelled, collecting on a filter the grey argillaceous sediment of comenamate of ammonium and colouring matter, and dissolving it in hot water; decomposing the solution with hydrochloric acid not in excess; and purifying the precipitated dark brown scales of impure comenamic acid by repeated crystallisation from hot water, and treatment with animal charcoal free from iron. The crystals contain 2 atoms water (18·81 per cent.), and give it off at 100° C. They dissolve sparingly in cold, more freely in hot water, forming a solution which reddens litmus strongly. The acid dissolves in boiling alcohol of ordinary strength, but is nearly insoluble in boiling absolute alcohol.

The acid is decomposed by boiling with *potash*, yielding ammonia and comenate of potassium. It dissolves readily in *hydrochloric acid* and other strong mineral acids, and is precipitated therefrom by ammonia in quantity rather less than sufficient for saturation, as comenamate of ammonium.

Comenamic acid is monobasic, the normal salts being $C^6(H^4M)NO^4$. There are also several basic salts. The *ammonium-salt*, $C^6H^4(NH^4)NO^4$ forms small grains made up of delicate needles nearly insoluble in cold water; their solution reddens litmus. The *potassium-* and *sodium-salts* crystallise readily and redden litmus. The normal *barium-salt*, $C^6H^4BaNO^4$, obtained by mixing a solution of the crystallised ammonium-salt with chloride of barium, forms crystals with 1 at. water, which redden litmus. A *basic barium-salt*, $C^6H^4BaNO^4.BaHO + \frac{1}{2}H^2O$, is formed, by mixing chloride of barium with an ammoniacal solution of comenamate of ammonium, as a white heavy precipitate, which gives off its water (2·83 per cent.) at 100° C. The aqueous acid left in contact with carbonate of barium forms the normal or the basic salt according to the relative quantities. With *lime*, it forms two salts of similar constitution.

The ammonium-salt forms, with acetate of *lead*, a heavy insoluble precipitate.

Comenamic acid imparts to *ferric salts* a deep purple colouring, which is destroyed by mineral acids, but reproduced by water.

The crystallised ammonium-salt forms a grey precipitate with sulphate of *copper*.

The ammonium-salt super-saturated with ammonia forms, with nitrate of *silver*, a yellowish flocculent, quickly blackening precipitate; and the crystallised ammonium-salt forms a white gelatinous precipitate, which is partially decomposed by boiling water.

Comenamate of Ethyl, *Comenamic ether*, *Comenamethane*, $C^8H^9NO^4 = C^6H^4(C^2H^5)NO^4$. (How. Ed. M. Phil. J. i. 212.)—When a solution of comenamic acid in absolute alcohol is treated with dry hydrochloric acid gas, and the liquid subsequently evaporated, there remains an oil which dries up at 100° C. to a solid mass, and when dissolved in alcohol, yields a *hydrochlorate of comenamic ether*, $C^8H^9NO^4.HCl + H^2O$; and on treating this compound with oxide of silver, or with ammonia (not in excess), comenamic ether is obtained in needle-shaped crystals containing 1 at. water, which they give off at 100° C., leaving the anhydrous ether.—When the solid mass above mentioned is treated with water, comenamic acid remains undissolved, and another portion of that acid separates as a crystalline powder from the solution, which contains hydrochloric acid.

The ether is neutral; melts to a yellow liquid when heated; is not altered by ammonia in the cold; and is converted by nitric acid into oxalate of ammonia. It dissolves sparingly in cold *water*, readily in hot water and in *mineral acids*, sparingly in *absolute alcohol*.

A compound of this ether with *hydriodic acid* is obtained by heating iodide of ethyl with a solution of comenamic acid in absolute alcohol to 150° C., in sealed tubes.

COMENIC ACID. $C^6H^4O^5 = \left.\begin{matrix}(C^6H^2O^3)'' \\ H^2\end{matrix}\right\} O^2$, or $C^{12}H^4O^{10} = C^{12}H^2O^8.2HO$. *Parameconic acid*, *Anhydrous Meconic acid*.—(Robiquet, Ann. Ch. Phys. [2] li. 326; liii. 428. Liebig, Ann. Ch. Pharm. vii. 237; xxvi. 116. Stenhouse, Phil. Mag. [3] xxv. 196. H. How, Ed. Phil. Trans. xx. [2] 225. Gm. xi. 328. Gerh. ii. 182.)

Comenic acid was discovered in 1832, by Robiquet, who at first regarded it as anhydrous meconic acid; it was afterwards recognised as a distinct acid by Liebig, who first observed the formation of carbonic acid which accompanies the conversion of meconic into comenic acid. It is produced: 1. By heating meconic acid to temperatures between 120° and 220° C., the change being attended with evolution of carbonic anhydride:

$$C^7H^4O^7 = C^6H^4O^5 + CO^2.$$

2. By continued boiling of meconic acid dissolved in water or in hydrochloric acid, likewise with evolution of carbonic acid. (Robiquet.)

Preparation.—Meconic acid or its potassium or barium-salt, is boiled with a strong mineral acid; or meconate of calcium is boiled with highly concentrated hydrochloric acid (Stenhouse); or acid meconate of potassium, produced by treating crude neutral meconate of calcium with very dilute hydrochloric acid, is heated with as much strong hydrochloric acid as is required to dissolve it (How), and the solution is left to crystallise. When the mere aqueous solution of the acid is boiled, too large a quantity of brown secondary product is formed. (Robiquet, Liebig.)

To purify the product, the still reddish crystals are dissolved in a slight excess of hot concentrated potash; the solution is filtered hot to separate a small quantity of lime; the white nodules which form on cooling are washed with a small quantity of cold water, till the strongly coloured mother-liquor is removed, then boiled with excess of hydrochloric acid; and the comenic acid which separates on cooling is freed from hydrochloric acid by two or three recrystallisations from water. The still remaining tinge of red may be removed by treatment with animal charcoal (Stenhouse). Or, the impure acid is dissolved in a quantity of boiling ammonia just sufficient to dissolve it (an excess, as well as continued boiling, causes the liquid to turn brown), and filtered immediately at the boiling heat; the yellow crystals which separate from the dark filtrate when left at rest, are washed with cold water and recrystallised from hot water; their pale-yellow aqueous solution is mixed with strong hydrochloric acid; and the comenic acid, which is precipitated in the form of a white or pale yellow powder, is crystallised from boiling water.

Properties.—Comenic acid forms anhydrous prisms, laminæ, or granules, having a very faint yellowish colour, requiring more than 16 pts. of *boiling water* to dissolve them; sparingly soluble in *hydrated alcohol*, but insoluble in absolute alcohol.

Decompositions.—1. The acid, when subjected to dry distillation, behaves like meconic acid (Robiquet). When comenic (or meconic) acid is quickly heated in a retort, above the temperature of 200° to 220° C., at which pyromeconic acid would be formed, but not till complete carbonisation takes place, an acid yellowish watery liquid passes over, having a faint empyreumatic odour; and there remains a blackish grey, porous, carbonaceous mass, from whose ammoniacal solution, after filtration, hydrochloric acid throws down thick dark green flakes, which, if exposed to the air after washing with water, shrink up to a substance resembling *glance-coal* in appearance, and in its chemical relations agreeing perfectly with metagallic acid (Winckler, *Repert.* 59, 42).—2. Comenic acid suspended in water through which a stream of *chlorine gas* is passed, forms a solution of chlorocomenic acid, which crystallises out after a while, and oxalic acid, which remains in solution:

$$C^6H^4O^5 + Cl^2 = C^6H^3ClO^5 + HCl.$$

The oxalic acid and a brown colouring matter which forms during evaporation must be regarded as secondary products (How).—3. Similarly, the colourless solution of comenic acid in *bromine-water* yields bromocomenic acid which crystallises, and oxalic acid (How).—4. *Nitric acid*, even when very dilute, converts comenic acid into carbonic, hydrocyanic, and oxalic acids; and if the nitric acid is tolerably strong, and heated at the beginning of the action, the process is complete in a few minutes (How).—5. *Strong sulphuric acid* acts upon comenic acid in the same manner as on meconic acid. (Robiquet).—6. The acid dissolved in water and boiled with excess of *ammonia* till nearly all the ammonia evaporates, forms a black-red liquid, which, on cooling, deposits impure comenamate of ammonium as a grey viscid sediment. (How, p. 96.)

COMENATES.—Comenic acid is dibasic, forming neutral or normal salts, $C^6H^2M^2O^5$, and acid salts, $C^6H^3MO^5$. The neutral comenates of the alkali-metals cannot be obtained in the solid state.

Acid Comenate of Ammonium, $C^6H^3(NH^4)O^5$, is obtained in How's process for purifying comenic acid. The aqueous acid slightly supersaturated with ammonia, and evaporated in vacuo over oil of vitriol, yields four-sided prisms having a yellowish tinge; they give off 9·04 per cent. (1 at.) water at 100° C. (Stenhouse). The salt forms white square prisms having a very strong lustre; they redden litmus even when they separate on cooling from a hot solution of the acid in excess of ammonia. They do not give off anything at 177° C., but at 199°, in a sealed tube, they melt and are converted into a black mixture of charcoal and comenamate of ammonium; their aqueous solution is also converted into this salt by continued boiling with ammonia (p. 1100). They dissolve readily in boiling water, sparingly in alcohol. (How.)

Comenates of Barium. a. *Neutral.* $C^6H^2Ba^2O^5 + H^2O$ (at 121° C.).—Chloride of barium mixed with a solution of the acid in excess of ammonia throws down immediately—or in very dilute solutions, after some time only—yellowish quadratic needles united in concentric groups. These crystals do not lose water at 100° C., but at 121°, they give off 19·03 per cent. water, and if then heated to redness in the air, burn away in a fiery cloud. They do not dissolve in boiling water, but when boiled with it, are converted into a basic salt, which does not give off water at 121° C., and contains 54·5 per cent. baryta. (How.)

β. *Acid salt.* $C^6H^3CaO^5$ (at 100° C.).—The free acid does not precipitate barium-salts (Stenhouse). The salt is produced when baryta is boiled with excess of the acid. Chloride of barium mixed with a cold-saturated aqueous solution of the crystallised ammonium-salt immediately forms a crystalline precipitate, and with a more dilute solution, gradually deposits transparent crystals, which give off their 20·86 per cent. (somewhat more than 3 at.) water at 100° C., and melt at a stronger heat. (How.)

Comenate of Calcium. a. *Neutral.* $C^6H^2Ca^2O^5 + H^2O$ (at 121° C.)—The acid supersaturated with ammonia, precipitates from chloride of calcium, if the solutions are saturated, very short prisms which give off 18·20 per cent. ($\frac{5}{2}$ at.) water at 121° C., and when the solutions are dilute, small shining crystals, which at 121° give off 31·37 per cent. ($5\frac{1}{2}$ at.) water. The two kinds of crystals are insoluble in water, but become basic when boiled with water.

β. *Acid salt.* $C^6H^3CaO^5$ (at 121° C.)—A mixture of chloride of calcium and a cold saturated aqueous solution of the crystalline ammonia-salt, quickly deposits transparent, shining, rhombic crystals, which give off their water slowly at 100°, but the whole, amounting to 26·15 per cent. ($\frac{7}{2}$ at.) at 121°. They dissolve readily in boiling water, and crystallise therefrom on cooling.

Comenate of Copper. $C^6H^2Ca^2O^5 + H^2O$ (at 100° C.)—The dark green aqueous mixture of cupric sulphate and comenic acid (or the crystallised ammonium-salt, according to How) deposits, after a few minutes, elongated pyramids having the colour of Schweinfurt green. No acid comenate of copper appears to exist. (How.)

Comenates of Iron. Ferric Comenate. $Fe^2O^3.4C^6H^4O^5 + 3H^2O$, or [if $fe = \frac{2}{3}Fe$] $= fe^2O.4C^6H^3feO^5 + 5H^2O$ (at 100° C.)—Comenic acid imparts a bright red colour to ferric salts. The dark blood-red mixture of ferric sulphate with a cold-saturated solution of comenic acid or its ammoniacal salt, becomes paler by long standing, and deposits small pitch-black, shining, very hard, nearly tasteless crystals, which grate between the teeth, yield a dark brown powder, and dissolve slowly both in cold and in hot water, forming a pale red solution. (Stenhouse.)

The red mixture of aqueous comenic acid with ferric sulphate, becomes dark yellow at 65° C. (and gives off carbonic acid, according to How), by conversion of all the sesquioxide of iron into protoxide at the expense of the acid, part of which at first remains undecomposed, so that a fresh portion of ferric sulphate again produces reddening. This colour, however, disappears when the liquid is digested for twelve hours with excess of ferric sulphate, in consequence of the complete conversion of comenic acid into *another acid;* hence the no longer red liquid deposits small, pale yellow, shining crystals of a ferrous salt (probably ferrous oxalate, as the liquid contains oxalic acid, according to How), which burn away when heated, and dissolve sparingly in water; the acid of these crystals extracted by potash no longer reddens ferric salts. (Stenhouse.)

Comenate of Lead.—The acid and its ammonia-salt form with neutral acetate of lead a yellowish white granular precipitate, soluble in excess of comenic acid, but not in acetic acid. (Stenhouse.)

A lead-salt examined by Robiquet contained 54·1 per cent. oxide of lead.

Comenates of Magnesium. α. *Neutral.* $C^6H^2Mg^2O^5 + \frac{3}{2}H^2O$ (at 100° C.)—Sulphate of magnesium forms with the acid saturated with ammonia, especially when the mixture is stirred, hard, closely adhering, crystalline grains, consisting of short microscopic needles. These crystals heated to 100°, slowly give off 26·50 per cent. (4 at.) water; and if then kept at 121° for four days, they give off such a quantity [nearly $\frac{3}{2}$ at.] that the residual salt contains 21·30 per cent. magnesia, and is therefore not quite anhydrous. They are not soluble in boiling water. (How.)

β. The *acid salt,* $C^6H^3MgO^5 + H^2O$ (at 100° C.), crystallises, after a while, from a mixture of sulphate of magnesium with the cold-saturated solution of the crystalline ammonia-salt, in small rhombs, and from more dilute solutions, on evaporation, in larger crystals, which are strongly acid, give off 22·08 per cent. (3 at.) water at 116°, and dissolve readily in hot water. (How.)

Comenic acid does not precipitate *mercuric chloride.* (Stenhouse.)

Comenates of Potassium. α. *Neutral.* $C^6H^2K^2O^5$.—The aqueous acid half neutralised with potash, so as to form the mono-potassic salt, yields no precipitate, but when completely neutralised, deposits the sparingly soluble dipotassic salt. In this respect, comenic acid is opposite to meconic acid, the acid potassium-salt of which is the less soluble of the two. (Robiquet.)

β. *Acid salt.* $C^6H^3KO^5$.—The acid, dissolved in a slight excess of boiling potash-ley, yields crystals on cooling, which, after washing with cold water, crystallise from hot water in short, square, anhydrous needles, which redden litmus. (How.)

Comenates of Silver.—The *neutral salt,* $C^6H^2Ag^2O^5$, is obtained by exactly precipitating a solution of nitrate of silver with comenic acid neutralised with ammonia. The thick yellow precipitate does not detonate when heated. (Liebig.)

The *acid salt,* $C^6H^3AgO^5$, is the precipitate (white, granular, or flocculent, according to Stenhouse) which the free acid produces in solution of nitrate of silver. (Liebig.)

Comenate of Sodium.—The solution of the acid in tolerably strong boiling soda-ley yields, on cooling, nodules and prisms, which, after washing with a little cold water, crystallise from the smallest possible quantity of hot water, in acid, anhydrous, four-sided prisms, containing 17·09 per cent. soda, and therefore = $C^6H^3NaO^5$. (How.)

Comenates of Strontium.—The neutral and acid salts closely resemble the corresponding barium-salt, but are more soluble.

Substitution-derivatives of Comenic Acid.

BROMOCOMENIC ACID. $C^6H^3BrO^5$. (How, *loc. cit.*)—The colourless solution of comenic acid in a slight excess of bromine-water deposits, after a few hours, oily, colourless, shining, strongly refracting, four-sided prisms, which dissolve in water and in alcohol less easily than chlorocomenic acid; they give off their water of crystallisation at 100° C.

The acid is decomposed by *nitric acid,* yielding hydrobromic, carbonic, hydrocyanic, and oxalic acids. With *zinc* and *water* it decomposes like chlorocomenic acid.

Bromocomenic is dibasic, like comenic acid. The *acid bromocomenates of ammonium, potassium,* and *sodium* are crystallisable; the first crystallises in long needles. The neutral salts of these bases are not obtainable.

The *neutral bromocomenates of barium* and *calcium* are amorphous and insoluble; the *acid* salts are very easily soluble.

The solution of the acid in a slight excess of ammonia yields, with nitrate of silver, neutral *bromocomenate of silver* in the form of a yellow precipitate having the consistence of clay when dry; and the solution of the acid in warm water forms with nitrate of silver, flakes of the *acid salt*, $C^6H^2AgBrO^5$, which crystallises from boiling water in short shining prisms.

CHLOROCOMENIC ACID. $C^6H^3ClO^5$. (How, *loc. cit.*)—Obtained by passing chlorine through water in which pulverised comenic acid is suspended, washing the crystals which separate with cold water, and recrystallising from hot water,—or by passing chlorine into cold water saturated with acid comenate of ammonium; the liquid then acquires the colour of chlorine-water, and gradually deposits crystals of chlorocomenic acid, which increase on addition of hydrochloric acid, and may be purified as in the first process. The mother-liquor becomes continually browner, and still deposits brown crystals of the acid.

The crystals are long, colourless, shining, four-sided prisms, containing 12·47 per cent. ($\frac{3}{2}$ at.) water, which they give off at 100° C. They dissolve both in cold and in hot *water*, more readily than comenic acid; very easily in warm alcohol.

The acid melts when heated, blackens, gives off a large quantity of hydrochloric acid, and at last yields a small crystalline sublimate, probably consisting of paracomenic acid. By *nitric acid* it is quickly converted into hydrochloric, carbonic, hydrocyanic, and oxalic acids. Its aqueous solution, treated with zinc, slowly gives off hydrogen, and afterwards contains hydrochloric acid and oxide of zinc.

Chlorocomenic acid is dibasic, forming *neutral salts*, $C^6HM^2ClO^5$, and *acid salts*, $C^6H^2MClO^5$.

The *chlorocomenates* resemble the comenates, but dissolve more readily in water.

The acid chlorocomenates of ammonium, potassium, and sodium crystallise readily. The neutral salts are not obtainable.

The ammonium-salt forms with *chloride of barium* and *chloride of calcium*, bundles of needles which appear more or less quickly, according to the degree of concentration; with *sulphate of magnesium*, it gradually forms a few crystals; and with *cupric sulphate*, immediately, a crystalline precipitate. The neutral chlorocomenates of these bases appear to be all amorphous and insoluble.

The acid colours *ferric salts* deep red, like comenic acid.

Silver-salts. a. Neutral.—The acid dissolved in a slight excess of ammonia forms, with nitrate of silver, yellow amorphous flakes, which, after drying, resemble clay in appearance, consistence, and tenacity. The salt dried at 100° C. contains 56·85 per cent. silver, and is therefore $C^6HAg^2ClO^5$. When ignited in the air, it leaves silver, together with a small quantity of chloride of silver; when boiled with hydrochloric acid, it remains partly undecomposed. It is insoluble in boiling water, but dissolves in nitric acid, from which, if heated with the salt, it separates cyanide of silver.

b. Acid.—The warm aqueous acid added to solution of nitrate of silver throws down feathery crystals, which, after washing with cold water, separate from boiling water in short shining needles. These crystals give off 4·44 per cent. water at 100° C When ignited, they leave silver and chloride of silver.

ETHYLCOMENIC ACID. $C^8H^8O^5 = C^6H^3(C^2H^5)O^5$ (How, *loc. cit.*).—To prepare this acid, dry hydrochloric acid gas is passed through absolute alcohol in which pulverised comenic acid is suspended, till the acid dissolves, which takes place slowly; the clear liquid (which deposits nothing on addition of water) is evaporated at a temperature below 100° C.; the crystalline residue is maintained at this temperature, till it no longer smells of hydrochloric acid, and then left to crystallise by cooling from its solution in water at nearly 100°. Or, pulverised comenic acid, heated with alcohol and iodide of ethyl in a closed vessel to a temperature above 100°, forms a granular deposit consisting of an acid not yet examined, and ethylcomenic acid, in needle-shaped crystals, which may be separated and purified by recrystallisation. Similar products are obtained by heating a mixture of comenic acid, alcohol, and chloride of amyl to 160° for 12 hours.

The acid forms large square needles, which begin to evaporate at 100° C.; melt at 135° into a clear brown-red liquid, which solidifies again in the crystalline form on cooling; and if kept for a longer time at 135°, sublime in long flat unaltered needles, having the same composition. It is very soluble in water and alcohol, and reddens litmus; the aqueous solution coagulates albumin.

The acid may be boiled for a short time without alteration, but if boiled for a longer time, it yields free comenic acid. With aqueous solutions of the fixed alkalis, even in the cold, it very quickly forms salts, and yields free alcohol.

When ammoniacal gas is passed through a solution of the acid in absolute alcohol, the *ammonia salt* is deposited in yellow silky bundles of needles, which give off ammonia in dry air, and almost completely in vacuo over oil of vitriol, leaving ethylcomenic acid.

The acid imparts a deep red colour to *ferric salts*. Its *silver-salt* is gelatinous, and decomposes very quickly, even in the dark.

COMPTONITE. See THOMSONITE.

CONCENTRATION. A process which has for its object to increase the amount of a dissolved substance in a liquid, relatively to the quantity of the solvent, without adding any more of the dissolved substance itself. When the solvent is volatile, this object is effected by evaporation, as when water, alcohol, or ether is expelled from a solution by heat, by exposure to the air, or in vacuo. If the dissolved substance is more volatile than the solvent, the concentration is effected by distillation, the more concentrated liquid being then found in the distillate, as in the rectification of hydrated alcohol and of volatile oils dissolved in water. In the case of aqueous liquids, concentration is sometimes effected by freezing out the water; in this manner, a strong solution of salt may be obtained from sea-water; strong spirit from vinous liquids, &c.

A similar principle is applied to the separation of silver from lead. The argentiferous lead is melted and left to cool, till about two-thirds of the mass is solidified; this consists of nearly pure lead, the portion which still remains liquid being an alloy richer in silver than the original mass. By repeating this operation several times, the alloy at last becomes sufficiently rich in silver to be treated by cupellation.

CONCHIOLIN. An organic constituent of the shells of certain molluscs, first observed by Frémy. It closely resembles keratin, or epidermose; does not yield gelatin by boiling with water, even under strong pressure; is insoluble in water, alcohol, ether, acetic acid, dilute mineral acids, and potash-ley. It contains 50 per cent. carbon, 6 hydrogen, and 16 to 16·7 nitrogen, a composition very near to that of epidermose: whether it contains sulphur does not appear to have been made out. A similar substance, but containing only 12 or 13 per cent. nitrogen, was found by Schlossberger in the byssus of acephalous molluscs.

CONCRETIONS, ANIMAL. This term is applied to all deposits in the animal body which are destitute of distinct organic structure. They are almost always of morbid character, a few only, as the brain-sand (the sabulous matter of the pineal gland), the crystals in the auditory organs of most animals, and in the vertebral column of frogs, appearing to occur in healthy animals.

Concretions are formed:—1. In the liquid secretions, as urinary, salivary, and biliary calculi, concretions in the stomach and intestines, in the lachrymal ducts, the cavity of the nose, the sebaceous glands of the skin (gouty concretions), &c.—2. In the cellular tissue of the organs, as in the brain, heart, veins, lungs, and indeed in all parts of the body. These latter are formed by the gradual transformation of other morbid products the animal matter of which is gradually absorbed, while the inorganic substance remains, and is often increased by addition of fresh deposits. All concretions of this kind have a very similar, indeed almost identical, constitution, consisting of a base sometimes predominant, sometimes subordinate, of coagulated fibrin, with deposits of phosphate and carbonate of calcium, ammonio-magnesian phosphate and carbonate of magnesium, in variable proportions. Another class of concretions allied to those last mentioned, are the so-called asteromatose deposits in the coatings of the arteries, especially of the aorta. They are sometimes, but not always, associated with calcareous deposits, and form layers of yellowish-white colour, and very slight consistence. They consist mainly of crystalline deposits of cholesterin.

The essential constituents of animal concretions are.

Uric acid and its salts.
Xanthin and cystin.
Hippurates and benzoates.
Cholesterin and fat.
Bile-pigment or cholochrome.
Fibrin.
Phosphate of calcium; ammonio-magnesian phosphate; oxalate of calcium; carbonate of magnesium.

The following substances occur as cements or less essential constituents: urinary and gall-bladder mucus, albumin, blood-red, the biliary acids, animal matter of indeterminate character, and sometimes soluble salts.

The chemical analysis of animal concretions must always be preceded by an examination of their physical structure. They are very often made up of concentric layers of substances differing in chemical constitution, so that it becomes necessary to make a separate analysis of each layer.

As respects their behaviour when heated, concretions are distinguished as—1. *Perfectly combustible.*—2. *Partially combustible.*—3. *Incombustible.* Their special chemical characters are given in the following tables. (Handw. d. Chem. ii. [2] 171.)

1. *Stones which burn without residue when heated on platinum-foil.*

a. The nitric acid solution is coloured red by ammonia, after evaporation.		*b*. The nitric acid solution is *not* coloured red by ammonia, after evaporation.		The substance burns with a bright flame.		The substance has a brown colour, is friable, like ochre, and burns with an animal odour.	
α. Does not give off ammonia when treated with potash.	β. Gives off ammonia when treated with potash.	Turns yellow on evaporation; insoluble in carbonate of potassium.	Turns dark brown on evaporation; soluble in ammonia and in carbonate of ammonia, crystallising from the former solution in microscopic six-sided tables.	Has a distinct crystalline texture; dissolves with aid of heat in alcohol, and crystallises from the solution, on cooling, in nacreous laminæ. Insoluble in caustic potash.	Emits, in burning, the odour of burnt horn, and swells up. Soluble in caustic potash, precipitated from the solution by acetic acid; soluble in excess of acetic acid, and then precipitable by ferrocyanide of potassium.	Sparingly soluble in alcohol and in water; soluble, with dark brown colour, in potash, the solution exhibiting, with nitric acid, the variations of colour characteristic of cholochrome.	Soluble in alcohol. The solution has a bitter taste, and exhibits a splendid violet-red colour with sugar and sulphuric acid.
Uric Acid.	**Urate of Ammonia.**	**Xanthin.**	**Cystin.**	**Cholesterin.**	**Fibrin.**	**Cholochrome.**	**Biliary Acids.**

2. *Stones which leave a considerable residue when heated on platinum-foil.*

1. The residue melts easily before the blowpipe.		2. The residue does not melt before the blowpipe.			3. The substance gives, with nitric acid and ammonia, the reaction of uric acid, but leaves a residue when ignited.			
α. Does not effervesce with acids, either before or after ignition; soluble in hydrochloric acid; precipitable by ammonia; precipitated by oxalate of ammonia. Black-brown enamel with cobalt-solution.	β. Gives off the odour of ammonia when heated; soluble without effervescence in acetic acid, and precipitated from this solution in the crystalline form by ammonia. Dark red glass with cobalt-solution.	α. Residue white, not alkaline; in other respects exhibiting the behaviour of neutral phosphate of calcium.	β. The fresh substance not attacked by acetic acid. Soluble without effervescence in mineral acids, and precipitated by ammonia; residue alkaline; effervesces with acids.	γ. Emits a strong white light when ignited; effervesces with acids before ignition; precipitated from the neutralised solution by oxalate of ammonia.	α. Melts before the blowpipe, and colours the flame deep yellow.	β. Behaves like α, excepting that it does not colour the flame yellow. Its solution in hydrochloric acid gives a yellow precipitate with dichloride of platinum.	γ. Infusible before the blow-pipe, and behaves, after ignition, like carbonate of calcium.	δ. Infusible before the blowpipe. The residue dissolves, with slight effervescence, in dilute sulphuric acid, and is precipitated from this solution by potash or by ammonio-sodic phosphate.
Neutral Phosphate of Calcium.	**Ammonio-magnesian Phosphate.**	**Basic Phosphate of Calcium.**	**Oxalate of Calcium.**	**Carbonate of Calcium.**	**Urate of Sodium.**	**Urate of Potassium.**	**Urate of Calcium.**	**Urate of Magnesium.**

CONDENSATION. This term, in its most general sense, implies increase of density, but it is often restricted to the passage of a gas to the liquid or solid state.

CONDRODITE. See CHONDRODITE.

CONDURRITE. A mineral containing copper and arsenic, originally obtained from the Condurrow mine near Helstone, in Cornwall; since found in the Huel Druid mine, near Redruth; also in mines at Coquimbo and Copiapo, Chili. It forms amorphous, roundish, flattened nodules, with flat conchoïdal fracture, brownish-black colour, bluish-black on the outer surface, opaque, dull or with glimmering lustre; streak metallic; powder brownish-black; soft. Specific gravity, 4·2—5·2.

Condurrite has been frequently analysed, but with very variable results; in fact it appears to be a mixture resulting from the alteration of Domeykite (Cu^6As), and mainly consisting of a hydrated cuprous arsenite mixed with small quantities of manganese, sulphur, iron, and silica. (Kopp, Handw. d. Chem. ii. [3], 173.)

CONGLOMERATE. A geological term applied to masses of rounded fragments of older rocks held together by a cement; if, on the other hand, the fragments are for the most part sharp-edged, the mass is called breccia. Conglomerates are distinguished as quartzose, calcareous, dolomitic, granitic, syenitic, &c., according to the nature of the component fragments: the cement may be siliceous, calcareous, or argillaceous.

ADDENDA.

ACETYLENE. C^2H^2. A gaseous hydrocarbon, which appears to have been first obtained by E. Davy (Records of gen. Sci. Nov. 1836; Gm. viii. 150), though in an impure state, by the action of water on the black substance which passes over in the preparation of potassium; but its preparation in the pure state, and indeed the establishment of its existence as a definite compound, is due to Berthelot (Institut, 1859, p. 410; 1860, p. 565; Rép. Chim. pure, ii. 222; Ann. Ch. Pharm. cxv. 116), who obtained it by passing ethylene-gas, or the vapour of ether, alcohol, aldehyde, or wood-spirit, through a red-hot tube, and by the action of red-hot copper on chloroform. Ether yields it in largest quantity, but by whichever of the preceding methods it is produced, it is always mixed with a considerable quantity of other gases, and requires to be purified by passing the gaseous mixture into an ammoniacal solution of cuprous chloride; a red precipitate is then formed which, when decomposed by hydrochloric acid, yields pure acetylene.

Berthelot has further shown that acetylene is one of the constituents of coal-gas, and that it may be formed by the direct combination of carbon and hydrogen, viz. by passing hydrogen gas over charcoal, heated to whiteness by the passage of the electric arc.

Acetylene is also produced: *a.* By the action of alcoholic potash on monobromethylene (vol. ii. 569), $C^2H^3Br - HBr = C^2H^2$ (Sawitsch, Compt. rend. lii. 157), or on bromide of monobromethylene ($C^2H^3Br^3$), bromacetylene, C^2HBr, being formed at the same time (Reboul, Ann. Ch. Pharm. cxxiv. 267).—*b.* By passing the vapour of monobromethylene into an ammoniacal solution of nitrate of silver, in which case a precipitate is formed consisting of the silver-compound of acetylene $C^2H^2Ag^2$ (more probably C^2HAg), which, when treated with dilute hydrochloric acid, yields acetylene (Miasnikoff, Ann. Ch. Pharm. cxviii. 330).—*c.* By heating monobromethylene with ethylate or amylate of sodium, the products being bromide of sodium, ethylic or amylic alcohol, and acetylene. (Sawitsch, see vol. ii. p. 569.)

$$\underset{\text{Bromethylene.}}{C^2H^3Br} + \underset{\substack{\text{Amylate of}\\ \text{sodium.}}}{C^5H^{11}NaO} = NaBr + \underset{\substack{\text{Amylic}\\ \text{alcohol.}}}{C^5H^{12}O} + \underset{\text{Acetylene.}}{C^2H^2}.$$

d. When a mixture of marsh-gas and carbonic oxide is passed through a red-hot tube. (Odling.)

$$CH^4 + CO = C^2H^2 + H^2O.$$

Acetylene is a colourless gas of specific gravity 0·92, having a peculiar and unpleasant odour, moderately soluble in water, not condensed by cold or pressure. It burns with a very bright and smoky flame, 1 vol. acetylene consuming 2½ vol. *oxygen*, and producing 2 vol. carbonic anhydride. When mixed with *chlorine*, it detonates almost instantly, even in diffused daylight, with separation of charcoal.

Acetylene unites with *copper* and with *silver*, forming detonating compounds, which are produced on passing the gas into the ammoniacal solutions of cuprous chloride and nitrate of silver respectively. The copper-compound is red, the silver-compound grey; both are decomposed by hydrochloric acid, with separation of acetylene. Acetylene mixed with air, and in presence of moisture, rapidly attacks metallic copper. The gas is absorbed and the copper becomes coated with a black deposit which explodes violently when heated. The formation of this substance (acetylide of copper mixed probably with cuprous oxide) is doubtless the cause of the dangerous explosions which sometimes occur in the cleaning out of copper gas-mains after long use. (Crova, Compt. rend. lv. 435; J. pr. Chem. lxxxvii. 124.)

Acetylene unites with *nascent hydrogen*, and is converted into ethylene C^2H^4. This change is brought about by subjecting the copper-compound of acetylene to the action of hydrogen evolved by the action of zinc on aqueous ammonia; the hydrogen evolved from acid liquids does not produce this reaction.

Acetylene unites, like ethylene, with *bromine*, *sulphuric acid*, and the elements of *water*, forming with bromine the compound $C^2H^2Br^2$, with sulphuric acid, acetyl-sulphuric acid $C^2H^2.H^2SO^4$, and with the elements of water, acetyl-alcohol $C^2H^2.H^2O = C^2H^4O$. (Berthelot.)

Acetyl-sulphuric acid, $C^2H^4SO^4$, is produced by brisk and long-continued agitation of acetylene with strong sulphuric acid. If the liquid be then carefully diluted, saturated with carbonate of barium, and the filtrate evaporated, acetyl-sulphate of barium is obtained in crystals. (Berthelot.)

Acetylic alcohol, $C^2H^4O = C^2H^2.H.O$, is obtained by distilling and rectifying the acid liquid just mentioned, as an easily decomposible liquid resembling acetone, but having an extremely pungent odour. It is somewhat more volatile than water, and is separated therefrom by carbonate of potassium, but apparently not by chloride of calcium. (Berthelot.)

Bromacetylene. C^2HBr. (Reboul, Compt. rend. lv. 136.)—Produced by the action of alcoholic potash on dibromide of dibromethylene:

$$C^2H^2Br^2.Br^2 - HBr - Br^2 = C^2HBr.$$

Also, together with acetylene and dibromethylene, by the action of boiling alcoholic potash on dibromide of monobromethylene.

$$\begin{array}{llll} C^2H^3Br.Br^2 & - \quad HBr & = & C^2H^2Br^2. \\ & & & \text{Dibromethylene.} \\ C^2H^2Br^2 & - \quad HBr & = & C^2HBr. \\ & & & \text{Bromacetylene.} \\ C^2HBr.Br^2 - HBr & - \quad Br^2 & = & C^2H^2. \\ & & & \text{Acetylene.} \end{array}$$

It is spontaneously inflammable, liquefies under a pressure of three atmospheres, is soluble in water, and very soluble in dibromethylene, whereas acetylene is much less soluble in that liquid. This property may be rendered available for the separation of acetylene and bromacetylene.

It unites with *bromine*, forming the dibromide of bromacetylene, $C^2HBr^3 = C^2HBr.Br^2$. When passed into ammoniacal solution of cuprous chloride, it yields a precipitate of cuprosacetylene, C^2HCcu:

$$C^2HBr + 3Cu^2Cl = C^2HCcu + CuBr + 3CuCl;$$

which, when treated with hydrochloric acid, yields a gas having the composition and most of the properties of Berthelot's acetylene, but differing somewhat in its behaviour to bromine, with which it yields the compound $C^2H^2Br^4$, and a small quantity of C^2HBr^3.

ALLYLENE. C^3H^4. This compound, homologous with acetylene, is produced, in like manner, by the action of ethylate of sodium on monobromotritylene, C^3H^5Br. The materials are made to react in a well-cooled, sealed flask, and on opening the vessel, a large quantity of gas escapes, which, when passed into an ammoniacal solution of cuprous chloride, produces a yellow precipitate. This precipitate decomposed by hydrochloric acid yields pure allylene, a colourless gas, having an unpleasant odour, burning with a smoky flame, and forming with *mercurous salts* a dark grey precipitate, and with *silver salts* a white precipitate which detonates when heated. The copper compound above mentioned burns with a reddish flame, and is decomposed with incandescence by bromine. (Sawitsch, Compt. rend. lii. 399; Ann. Ch. Pharm. cxix. 185.)

Allylene is also produced by passing the vapour of bromotritylene into a hot concentrated alcoholic solution of potash. The gas thus evolved forms in ammoniacal silver-solution, a precipitate consisting of a dark yellow compound, *silver-acetylene*, and a heavier white compound which is *silver-allylene*, $C^3H^4Ag^2$. The gas evolved from this compound by the action of hydrochloric acid, forms with bromine an oily liquid, which boils, with partial decomposition, between 180° and 200° C., and has the composition of a mixture of $C^3H^4Br^2$ and $C^3H^4Br^4$. (Morkownikoff, Bull. Soc. Chim. 1861, p. 90.)

CÆSIUM. *Symbol*, Cs. *Atomic weight*, 133.—A metal belonging to the same group of elements with lithium, sodium, potassium and rubidium. Its existence was detected in 1860 by Kirchhoff and Bunsen, by help of the method of *spectral analysis* which they introduced (see SPECTRUM, SPECTRAL ANALYSIS). The compounds of cæsium so closely resemble the corresponding compounds of potassium and rubidium, that no difference can be perceived between them by ordinary analytical means; but in the spectrum-apparatus a few thousandths of a milligramme can easily be detected. The most characteristic lines in the cæsium-spectrum are two blue lines Cs α and Cs β, in the neighbourhood of the strontium-line, Sr δ; they can be clearly seen, even with silicate of cæsium, and the name *Cæsium*, from *cæsius*, sky-blue, has been chosen as recalling their colour.

Cæsium has not yet been found, except in company with rubidium (see Rubidium), and it occurs in even still smaller quantities than the latter element. Cæsium was first detected in the Dürkheim mineral water, ten kilogrammes of which contain not quite two milligrammes of chloride of cæsium. Kreuznach water contains less, and in the lepidolite of Rozena (which is the principal source of rubidium) only insignificant traces of it are found. (Kirchhoff and Bunsen, Pogg. Ann. cxiii. 353; Jahresber. 1861, 177.)

The most abundant source of it yet discovered appears to be the lepidolite of Hebron, in Maine, U.S. This mineral occurs there in large quantity in a coarsely crystalline granite, associated with red and green tourmaline and albite. It has a granular, and at the same time foliated crystalline structure, a pale rose to violet colour, and very closely resembles the lepidolite of Penig, in Saxony, and, like that, is also associated with the rare species, amblygonite. It contains rather more than 0·3 per cent. of cæsium, and as much rubidium as the lepidolite of Rozena. (O. D. Allen, Phil. Mag. [4] xxv. 189.)

Cæsium has also been found, in comparatively large quantity, in the mineral waters of Baden-Baden (Bunsen), Bourbonne-les-Bains, Haute-Marne (Grandeau, Ann. Ch. Phys. [3] lxvii. 177), in the *salines* of Aussee, and in the lithium-mica of Zinnwald (Schroetter, Wien Akad. Ber. xliv. 218). It exists in perceptible, but generally very small, quantities, in several other minerals, as triphyline (Blake, Sill. Am. J. [2] xxxiii. 274; Grandeau), carnallite (Erdmann), petalite (Grandeau), in the mineral water of Vichy (Grandeau), in those of Topusco and Lassinja (Schneider, Wien Akad. Ber. xlv. 483), and in the *salines* of Ebensee. (Redtenbacher, *ibid.* xliv. 153.)

The separation of cæsium from sodium and potassium depends upon the exceedingly slight solubility in water of its chloroplatinate. In order to obtain it pure, it is precipitated, together with chloride of potassium and chloride of rubidium, by means of chloride of platinum, from the mother-liquor, freed from everything except alkaline salts, obtained by the evaporation of Dürkheim water (Bunsen operated with the residue of about 40,000 kilogrammes of water); the precipitate is boiled with a *very small* quantity of water, allowed to settle, and the still hot solution decanted; when this operation has been repeated twenty times, the mixture of chloroplatinates of cæsium and rubidium which remains undissolved is reduced by heating in a stream of hydrogen, and the chlorides of those metals are extracted from the residue by boiling water. To separate the rubidium, the chlorides are transformed into carbonates, and the dry mixture of salts repeatedly exhausted with absolute alcohol, in which carbonate of cæsium is soluble, but carbonate of rubidium insoluble. As the carbonate of cæsium so obtained may still contain small quantities of potassium and rubidium, it must, for complete purification, be treated with sufficient baryta-water to render about four-fifths of it caustic, evaporated in a platinum dish, and the residue extracted with the smallest possible quantity of alcohol, which dissolves hydrate of cæsium, but leaves the carbonates of potassium and rubidium behind. When this operation has been repeated until the product, examined in the spectrum-apparatus, no longer gives the potassium and rubidium reactions, or gives them only very faintly indeed, the further treatment of it is found not to alter its equivalent weight; although the salt thus obtained is still a mixture of the chlorides of cæsium and rubidium, and not pure chloride of cæsium, as Bunsen at first supposed (*vid. infr.*).

The following process is given by Allen (*loc. cit.*) for the extraction of cæsium from the lepidolite of Hebron. Ten parts of the mineral, pulverised until it will pass through a sieve of 20 holes to the linear inch, are mixed with forty parts of coarsely powdered quicklime; a quantity of water sufficient to slake the lime is next mixed with as much hydrochloric acid as will convert from six to seven parts of the lime into chloride of calcium; the two mixtures are then united, and stirred vigorously during the slaking, thus intimately blending the mineral with suitable proportions of dry hydrate of lime and chloride of calcium. The mixture is put into Hessian crucibles, and heated to redness for six or eight hours (a shorter time would probably suffice). During the ignition, care must be taken to prevent the heat rising much above redness, as loss would then occur by volatilisation of the alkaline chlorides, and by the fusion of the mass and its consequent absorption into the crucibles. The product of this operation is detached from the crucibles, and boiled with water till all but a trace of the chlorides is removed. The solution thus obtained, containing chloride of calcium and alkaline chlorides, is evaporated till crystals begin to form; sulphuric acid is then added as long as sulphate of calcium separates, excess of acid being avoided, and the whole mass is evaporated to dryness, and strongly heated, to expel free hydrochloric acid. The residue is treated with water, the small quantity of sulphate of calcium which passes into solution is precipitated by carbonate of ammonium, the precipitate is filtered off, and the filtrate is again evaporated to dryness and ignited. In this way a mixture of the chlorides, containing also small quantities of the sulphates, of sodium, lithium, potassium, rubidium, and cæsium is obtained, from which the chlorides of the last two metals can be separated by treatment with bichloride of platinum as directed by Bunsen.

For the separation of cæsium from rubidium, Allen recommends the following process. The chlorides of the two metals are converted into sulphates, and then into carbonates, by precipitating with caustic baryta and saturating the solution with carbonic acid. From the carbonates, the acid tartrates are prepared by adding to the solution twice as much tartaric acid as is necessary to neutralise it, and these salts can then be separated from each other by fractional crystallisation: acid tartrate of rubidium requires for solution about eight times as much water as does acid tartrate of cæsium, and therefore crystallises out first, while the latter salt accumulates in the mother-liquors. The salts of the two alkalis may be thus separated from each other so completely that neither shows any trace of the presence of the other when examined with the spectroscope.

Pure **metallic cæsium** has not yet been obtained, but an amalgam of cæsium can be easily procured by electrolysing a solution of chloride of cæsium, using mercury as the negative pole. Cæsium-amalgam decomposes water in the cold, and when exposed to the air, gets hot and covers itself with a coating of deliquescent hydrate of cæsium. When cæsium-amalgam is connected with potassium-amalgam or with rubidium-amalgam and water, so as to form a galvanic circuit, it shows itself to be more electropositive than either of them; cæsium is therefore the most electropositive element yet known.

Bromoplatinate of Cæsium readily separates, together with the rubidium-salt, when dibromide of platinum is added to a dilute solution of the chlorides of the two metals. If potassium is present, the bromoplatinate of that metal is carried down likewise. (Allen.)

Carbonate of Cæsium, $Cs^2CO^3 + aq.$—Confusedly developed crystals, which give an anhydrous sandy powder when heated. Dissolves in 9·1 pts. absolute alcohol at 19° C., and in 5 pts. at 78·4° C.; very caustic; deliquesces in the air and gradually becomes converted into acid carbonate; dissolves in water in nearly all proportions with the aid of heat.

Acid carbonate of Cæsium, $CsHCO^3$.—Tolerably well-formed, but not measurable prismatic crystals, permanent in the air, of a glassy lustre. Reacts hardly alkaline; by ignition it is easily changed into the neutral salt.

Chloride of Cæsium, $CsCl$.—Crystallises in cubes, which deliquesce in the air like chloride of lithium, and can thereby be distinguished from chloride of potassium or of rubidium. When gently ignited, chloride of cæsium easily melts; it is somewhat volatile, and in the air easily becomes somewhat alkaline. (Bunsen.) According to Johnson and Allen pure chloride of cæsium is not deliquescent.

Chloroplatinate of Cæsium, $CsCl\,PtCl^2$.—Bright yellow sandy powder, composed of shining, transparent, microscopic regular octahedrons. It is more difficultly soluble than the chloroplatinate of either potassium or rubidium; the following table gives the solubility in 100 pts. water of the three salts, as determined by Bunsen, the

Temperature.	Potassium-salt.	Rubidium-salt.	Cæsium-salt.
0° C.	0·74	0·184	0·024
10	0·90	0·154	0·050
20	1·12	0·141	0·079
30	1·41	0·145	0·110
40	1·76	0·166	0·142
50	2·17	0·203	0·177
60	2·64	0·258	0·213
70	3·19	0·329	0·251
80	3·79	0·417	0·291
90	4·45	0·521	0·332
100	5·18	0·634	0·377

cæsium-salts having been purified by the first process, and therefore still containing a little rubidium.

Hydrate of Cæsium, CsHO + aq.—Confusedly crystallised, deliquescent, exceedingly caustic. At a red heat it does not become anhydrous; it attacks platinum, is entirely volatile when heated on a platinum wire, and is easily soluble in alcohol.

Nitrate of Cæsium, $CsNO^3$.—Contains no water of crystallisation, is isomorphous with nitrate of rubidium and not with nitrate of potassium. The crystals are hexagonal prisms combined with the hexagonal pyramid. P : P in the terminal edges = 142° 56′; in the lateral edges = 78° 58′. Rates of axes, 1 : *c* = 1 : 0·7135.

$$P \,.\, \infty P \,.\, P2 \,.\, \infty P2 \,.\, 0P \,.\, \tfrac{3}{4}P.$$

The salt has a cooling saline taste, like that of saltpetre, and is soluble in ten times its weight of water at 3° C. (Bunsen.)

Picrate of Cæsium resembles the corresponding potassium-salt. It cannot be separated from picrate of rubidium by crystallisation. (Allen.)

Sulphate of Cæsium, Cs^2SO^4, forms anhydrous, ill-defined, hard crystals, grouped together in bunches, and permanent in the air. One part of the salt dissolves in 0·63 pts. of water at − 2° C. (1 pt. of sulphate of potassium dissolves in 12·5 pts. of water at the same temperature.)

Sulphate of cæsium forms double salts with sulphate of magnesium, sulphate of cobalt, &c., belonging to the type $KMgSO^4 + 3H^2O$, and is isomorphous with the corresponding potassium- and ammonium-compounds. $CsCoSO^4 + 3H^2O$, shows the following surfaces: $0P \,.\, \infty P \,.\, +P \,.\, [P\infty] \,.\, +2P\infty \,.\, \infty P2$. Sulphate of cæsium forms, with sulphate of aluminium, an alum crystallising in regular octahedrons of a glassy lustre. (Bunsen, Ann. Ch. Pharm. cxix. 111.)

Acid tartrate of Cæsium, $C^4H^5CsO^6$.—Colourless, transparent, flattened prisms, which do not diminish in weight when pulverised and dried at 100°. One part of this salt dissolves in 1·02 pts. of boiling water, or in 10·32 pts. of water at 25° C. (Allen.) The *neutral tartrate* is very deliquescent. (Bunsen.)

Atomic weight of Cæsium.—The atomic weight of cæsium has been determined by the analysis of its chloride. This salt, purified from chloride of rubidium by means of chloride of platinum in the manner already described, was found by Bunsen to contain:—

	Chlorine.	Cæsium.
After the 1st purification, ...	22·334	77·666
„ 2nd „	22·334	77·666
„ 3rd „	22·316	77·684

whence he deduced 123·4 for the atomic weight of cæsium. Subsequent experiments by Johnson and Allen (Phil. Mag. [4] xxv. 196) have shown that the chloride of cæsium used for these determinations still contained chloride of rubidium, and that the atomic weight calculated from them is consequently too low. Their analyses of chloride of cæsium, prepared from the acid tartrate purified by concentrating its solution and recrystallisation, gave the following results:—

	Chlorine.	Cæsium.
I.	21·044	78·956
II.	21·031	78·969
III.	21·043	78·957
IV.	21·063	78·937

Bunsen has since published new determinations (Pogg. Ann. cxix. 1) which agree very closely with these. The chloride of cæsium used for them was prepared by the following process, from a mixture of the chlorides of cæsium and rubidium which had been previously completely freed from potassium, sodium, and lithium. The chlorides were first converted into carbonates, and then a little more tartaric acid was added to the solution than was needed to convert the cæsium into neutral tartrate and the rubidium into the acid salt (the quantity of acid requisite being deduced from a preliminary determination of the amount of chlorine in the mixed chlorides). The liquid was next evaporated to dryness, and the powdered saline mass exposed to moist air in a funnel stopped with a small filter. In this way a solution of the very deliquescent tartrate of cæsium was obtained, while the acid tartrate of rubidium remained as a solid salt in the funnel. The tartrate of cæsium was converted into chloride, precipitated with bichloride of platinum, the precipitate washed and decomposed by heating in a stream of hydrogen, and this process was repeated until the proportion of chlorine in the resulting chloride of cæsium did not alter any longer. The product so prepared gave—

	Chlorine.	Cæsium.
After the 4th purification, ...	21·057	78·943
" 5th "	21·045	78·955
" 6th "	21·052	78·948

Taking Ag = 107·94 and Cl = 35·46 (Stas), the mean of Johnson and Allen's experiments gives 133·03 for the atomic weight of cæsium, while the mean of Bunsen's most recent experiments gives 132·99, so that we may take Cs = 133·0 as being very near the truth.

On the spectrum of cæsium, see Johnson and Allen (Phil. Mag. [4] xxv. 199), and Bunsen (Pogg. Ann. cxix. 6).—G. C. F.

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